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Review

Exposure of engineered nanomaterials to plants: Insights into the physiological and biochemical responses-A review☆

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A B S T R A C T

Recent investigations show that carbon-based and metal-based engineered nanomaterials (ENMs), components of consumer goods and agricultural products, have the potential to build up in sediments and biosolid-amended agricultural soils. In addition, reports indicate that both carbon-based and metal-based ENMs affect plants differently at the physiological, biochemical, nutritional, and genetic levels. The toxicity threshold is species-dependent and responses to ENMs are driven by a series of factors including the nanomaterial characteristics and environmental conditions. Effects on the growth, physiological and biochemical traits, production and food quality, among others, have been reported. However, a complete understanding of the dynamics of interactions between plants and ENMs is not clear enough yet. This review presents recent publications on the physiological and biochemical effects that commercial carbon-based and metal-based ENMs have in terrestrial plants. This document focuses on crop plants because of their relevance in human nutrition and health. We have summarized the mechanisms of interaction between plants and ENMs as well as identified gaps in knowledge for future investigations.

Contents

Abbreviations: n, prefix to denominate "nano"; μ, prefix to denominate "micro"; NP, nanoparticle; NM, nanomaterial; ENP, engineered nanoparticle; ENM, engineered nanomaterial; ppm, parts per million (mg/kg, mg/L); ZVI, zero-valent iron; CNT, carbon nanotube; SWCNT, single walled carbon nanotube; SWCNH, single walled carbon nanohorn; MWCNT, multi-walled carbon nanotube; OD, outer diameter; ID, inner diameter; NS, nutrient solution; MS, Murashige and Skoog; JPL, Jouanneau and Péaud-Lenoël; DNA, deoxyribonucleic acid; RAPD, random amplified polymorphic DNA; ROS, reactive oxygen species; H_2O_2, hydrogen peroxide; ABA, abscisic acid; ADH, alcohol dehydrogenase; APX, ascorbate peroxidase; CAT, catalase; GDH, glutamate dehydrogenase; GS, glutamine synthetase; GPT, glutamic-piruvic transaminase; IAA, indole-3-acetic acid; MDA, malondialdehyde; POD, peroxidase; SOD, superoxide dismutase; PSII, photosystem II; NOM, natural organic matter; wt, weight; TEM, transmission electron microscope; EC_{50}, half maximal effective concentration; IC_{50}, inhibition concentration, response reduced by half.

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1. Introduction

The “Nano-era” began in the early 2000s when more than 35 countries initiated research programs in nanotechnology, leading to a steady increase in production of engineered nanomaterials (ENMs) (Roco, 2003). Special characteristics of ENMs such as higher surface area to volume ratio and reactivity, compared with equivalent bulk materials, have allowed their utilization in different technologies. Manufacturing, electronics, communications, medicine, water and wastewater treatment, personal care, agriculture and food packaging technologies are using ENMs, including carbon-based (fullerenes, graphene, and carbon nanotubes (CNTs)) and metal-based (quantum dots, metal and metal oxide) ENMs (Klaine et al., 2008; Peralta-Videa et al., 2011; Roco et al., 2011; Bandyopadhyay et al., 2013). The intensive use of ENMs has raised concerns about their possible build up in ecosystems and food supply. Concerns are greater in agriculture, where soils are intentionally exposed to products containing ENMs, irrigated with raw wastewater, or amended with ENM-loaded biosolids (Shah et al., 2010; Lu et al., 2012; Colman et al., 2013; Hong et al., 2013; Gardea-Torresdey et al., 2014).

Plants, primary producers in terrestrial ecosystems, have evolved in environments that have a high load of naturally occurring nanomaterials such as in the vicinity of active volcanoes (Rico et al., 2011). However, agricultural regions have higher risk of exposure to ENMs than to naturally occurring nanoparticles (NPs), since thousands of tons of ENMs are predicted to be released into air, water, and soil (Keller and Lazareva, 2014). Quantum dots (QDs), carbon-based, and metal-based ENMs have been shown to produce different effects on plants (Rico et al., 2015b). These include accumulation, effects on the growth, physiological and biochemical traits, production, and quality of food, among others (Gardea-Torresdey et al., 2014). Quantum dots have been studied for cell imaging in living plants (Müller et al., 2006; Hu et al., 2010) given their fluorescent properties (Al-Salim et al., 2011). While mercaptoacetic acid (MAA)-coated CdSe/ZnS QDs had “very little” toxicity in maize seedlings (Hu et al., 2010), pristine cadmium/tellurium (Cd/Te) QDs have been found to cause fracture of chromatin, destruction of mitochondria and growth inhibition in green gram sprouts (*Phaseolus radiatus*) (Song et al., 2013a,b).

A good understanding of the interactions between ENMs and plant systems is of paramount importance for assessing the NMs' toxicity and their possible trophic transport (Gardea-Torresdey et al., 2014). Variation in accumulation and biotransformation, perturbation of agronomic and physiological traits, and detoxification ways have been reported (Ma et al., 2015). A few studies have also shown that ENMs impact seed quality in some plant species (Rico et al., 2014, 2015a; Majumdar et al., 2015). In addition, Rico et al. (2015b) reviewed the effects of metal-based ENMs on plants' antioxidant defense, while Ma et al. (2015) reviewed recent advances in ENMs' detoxification pathways in higher plants. In this review we analyze the most recent advances in the physiological and biochemical responses of higher plants to ENMs exposure. The reviewed literature covers the most used carbon-based and metal-based ENMs (ordered by their appearance in the periodic table, followed by stable metal oxides) and studies performed in model wild plants and crop plants.

2. Carbon-based nanomaterials

Carbon-based nanomaterials started in 1985 with the detection of the first fullerene, which was called “Buckminsterfullerene or the buckyball” (Kroto et al., 1985; Klaine et al., 2008). The CNTs are fullerene derivatives that appeared in 1991, while graphene was isolated in 2004 (Novoselov et al., 2004; Klaine et al., 2008). The three members of the CNT family have been found to interact with living organisms in different manners. Readers interested in the bioaccumulation and ecotoxicity of CNTs in aquatic microorganisms, pelagic invertebrates and vertebrates, and terrestrial invertebrates will find abundant information in the review by Jackson et al. (2013). Literature shows that, in plants, single walled carbon nanohorns (SWCNHs), SWCNTs, and multi-walled carbon nanotubes (MWCNTs) affect the physiology and biochemistry in diverse ways. Single-walled carbon nanotubes (SWCNTs) affect root growth in a species-dependent manner (Cañas et al., 2008). Besides the effects on plant growth (Khodakovskaya et al., 2013), research points towards the fact that all carbon-based ENMs could potentially modify the expression level of genes involved in responses to stimuli. For instance, SWCNHs impact the expression of genes involved in stress responses in tomato, a feature that can be controlled to regulate plant development (Lahiani et al., 2015). However, more studies especially related to food quality are required before recommending SWCNHs or other carbon based NMs to be safely used in crop production. On the other hand, CNTs have shown to modify DNA structure in plant tissues. While MWCNTs prompted chromosomal aberrations in *Allium cepa* roots, which resulted in differential expression of genes involved in cellular division and apoptosis (Ghosh et al., 2011), the proximity of SWCNT to DNA led to the unzipping of the strands, impairing the normal matching of the nucleobases in rice DNA (Katti et al., 2015).

Other biochemical changes induced by carbon-based ENMs include redox modifications in certain ions like Fe^{2+}or Fe^{3+} or cationic exchange in the maize (*Zea mays*) cell wall matrix (Tiwari et al.,2014). A previous compilation of the literature on carbon-based ENMs was published by Husen and Siddiqi (2014). Table 1 provides a summary of compelling data on the biochemical and physiological effects produced by carbon-based ENMs in plants. As seen in Table 1, most of the studies have been performed with MWCNTs. These nanotubes have been exposed to several plants such as zucchini, corn, tomato, and soybean with no apparent toxic effects (De La Torre-Roche et al., 2013). Similar results were reported by Lin and Xing (2007) in rape (*Brassica napus*), radish (*Raphanus sativus*), ryegrass (*Lolium perenne*), lettuce (*Lactuca sativa*), corn (*Zea mays*), and cucumber (*Cucumis sativus*). However, in