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Review

Engineered nanomaterial-mediated changes in the metabolism of terrestrial plants

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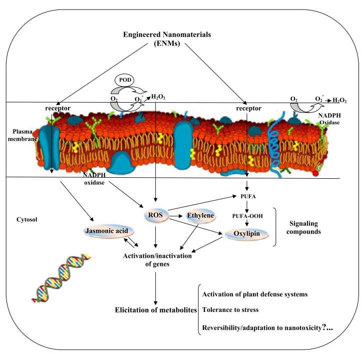
HIGHLIGHTS

- Engineered nanomaterials (ENMs) can enter plant cells through different pathways.
- They interact with intracellular structures and metabolic pathways.
- ENMs can have diverse effects on photosynthesis, photochemical fluorescence and quantum yield.
- Several classes of primary and secondary metabolites have been shown to be elicited.

GRAPHICAL ABSTRACT



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ABSTRACT

Engineered nanomaterials (ENMs) possess remarkable physicochemical characteristics suitable for different applications in medicine, pharmaceuticals, biotechnology, energy, cosmetics and electronics. Because of their ultrafine size and high surface reactivity, ENMs can enter plant cells and interact with intracellular structures and metabolic pathways which may produce toxicity or promote plant growth and development by diverse mechanisms. Depending on their type and concentration, ENMs can have positive or negative effects on photosynthesis, photochemical fluorescence and quantum yield as well as photosynthetic pigments status of the plants. Some studies have shown that ENMs can improve photosynthetic efficiency via increasing chlorophyll content and light absorption and also broadening the spectrum of captured light, suggesting that photosynthesis can be nano-engineered for harnessing more solar energy. Both up- and down-regulation of primary metabolites such as proteins and carbohydrates have been observed following exposure of plants to various ENMs. The potential capacity of ENMs for changing the rate of primary metabolites lies in their close relationship with activation and biosynthesis of the key enzymes. Several classes of secondary metabolites such as phenolics, flavonoids, and alkaloids have been shown to be induced (mostly accompanied by stress-related factors) in plants exposed to different ENMs, highlighting their great potential as elicitors to enhance both quantity and quality of biologically active secondary metabolites. Considering reports on both positive and negative effects of ENMs on plant metabolism, in-depth studies are warranted to figure out the most appropriate ENMs (type, size and optimal

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concentration) in order to achieve the desirable effect on specific metabolites in a given plant species. In this review, we summarize the studies performed on the impacts of ENMs on biosynthesis of plant primary and secondary metabolites and mention the research gaps that currently exist in this field.

Contents

1. Introduction . . . 276
2. Entry of ENMs into plant tissues and their interactions with cells . . . 276
 2.1. Engineered nanomaterials and photosynthesis . . . 279
3. Engineered nanomaterials and primary metabolism . . . 280
4. Engineered nanomaterials and elicitation of secondary metabolism . . . 282
5. Conclusions and future perspectives. . . . 287
References. . . . 288

1. Introduction

Nanoscale science and technology is the study and application of small sized objects range from 1 to 100 nm (nm), where novel characteristics make new and wide uses possible (US Environmental Protection Agency, 2007). Nanomaterials are therefore characterized as natural or engineered substances with at least one dimension in the size <100 nm. With quite diverse appearance, engineered nanomaterials (ENMs) can be spherical or near-spherical, tubular, or irregularly (non-spherical) shaped, which have been found in single, fused, and agglomerated forms with compositionally homogenous or heterogeneous. ENMs have superior properties over their bulk counterparts in that they exhibit much greater specific surface area to volume ratio, greater reactivity and mobility, and are subject to quantum confinement due to their ultrafine size (Service, 2003).

ENMs are manufactured for various applications and mainly include the following types: (1) carbon-based nanomaterials such as carbon nanotubes (CNTs), graphene and fullerenes (C60 and C70); (2) metal-based nanomaterials including zero-valent metals (such as Au, Ag, and Fe ENMs), metal oxides (such as nano-ZnO, $-TiO_2$ and $-CeO_2$), and metal salts (such as nano silicates and ceramics); (3) quantum dots (such as CdSe and CdTe); (4) nanosized polymers (including dendrimers and polystyrene).

ENMs can be released into the environment through recycling or waste during their manufacture and application deliberately (Liu et al., 2009; Mauter and Elimelech, 2008; Torney et al., 2007) or accidentally (Barnard, 2010). The rapidly increasing applications of ENMs have raised concerns regarding their potential effects on living organisms and non-living (abiotic) components of ecosystems. Plants are a vital component of ecological systems and serve both as important ecological receptors and as a potential route for the transport and bioaccumulation of ENMs into food chain at different trophic levels (Zhu et al., 2008). Hence, plants are regarded as one of the core groups of organisms that will be directly impacted by ENMs leaked or released into the environment because they directly interact with biosphere components. Studies performed using advanced techniques of detection have demonstrated that ENMs can be easily absorbed by plants germinated or grown in nutrient solutions (Irin et al., 2012; Khodakovskaya et al., 2012; Villagarcia et al., 2012) or soil (Rico et al., 2015a) supplemented with nano-sized materials, which can alter fundamental metabolic processes leading to different impacts on plant metabolism.

Metabolism is the whole range of chemical and physical processes within the cells of living organisms that could happen spontaneously (releasing energy) or non-spontaneously (requiring energy). Metabolic events are enzyme-catalyzed reactions that enable living organisms to grow, respond to biotic and abiotic factors surrounding them, remain healthy and maintain their structures, and reproduce. Metabolites are the intermediates and products of metabolic reactions. Plant metabolites are divided into primary and secondary metabolites based on their function and biosynthetic pathways. Plant primary metabolites are the organic substances that are directly deal with biological processes such as growth, development, and reproduction, and belong to diverse compound families including carbohydrates, amino acids, nucleic acids, lipids, organic acids and, steroids. Typically, secondary metabolites are not directly involved in the normal growth, development, or reproduction of plants, but usually have important ecological functions and play imperative roles in protecting plants against pests, diseases and various environmental stresses. Secondary metabolites are synthesized from primary metabolites by specialized reactions catalyzed by different enzymes. Generally, plant secondary metabolites can be divided into three large chemical classes: i) terpenes: composed almost entirely of carbon and hydrogen; ii) phenolics: generally made from simple sugars, have benzene rings, oxygen and hydrogen; iii) nitrogen containing compounds (alkaloids) (Bourgaud et al., 2001). These natural metabolites are sources of the bioactive compounds used in pharmaceuticals, drugs, cosmetics and fragrances.

A review of the literature shows that ENMs can have positive, negative, or neutral impacts on plants growth and development, but the mechanisms behind the aforesaid effects of ENMs are not fully clear and need to be explored further. Although a large number of studies carried out on the interaction of ENMs with plants in recent years, relatively little attention has been turned to the effect of different ENMs on plant metabolism. Therefore, in this review we put emphasis on the interactions occur between ENMs and the fundamental processes of primary and secondary metabolism in plants.

2. Entry of ENMs into plant tissues and their interactions with cells

As mentioned above, the application domain of ENMs has been expanded in various areas due to their unique characteristics including large surface area-to-volume ratio, ability to engineer electron exchange, and highly surface reactive capabilities. However, our knowledge of the direct interactions between ENMs and plant cells is relatively new (Hu et al., 2015a; Hu et al., 2015b; Dallavalle et al., 2015).

To fully understand ENMs interaction with plants, it is important to deeply characterize the penetration, translocation, accumulation and fate of these materials within plant cells and organelles such as chloroplasts.

ENMs uptake in plants have been detected and confirmed using different techniques such as transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), scanning transmission X-ray microscopy-near edge X-ray absorption fine structure spectroscopy (STXM-NEXAFS) (Ma et al., 2011), atomic force microscopy (AFM) (Ghosh et al., 2010), TEM X-ray microanalysis (Marchiol et al., 2014), X-ray fluorescence microscopy (XRF), confocal microscopy (CM), light microscopy (LM) (Kurepa et al., 2010), two-photon excitation