# **14 Nanomaterials Act as Plant Defense Mechanism**

## Ram Prasad, Nomita Gupta, Manoj Kumar, Vivek Kumar, Shanquan Wang, and Kamel Ahmed Abd-Elsalam

#### **Abstract**

Plants symbolize the prevalent edge between the environment and biosphere, so discovering how nanomaterials affect them is particularly significant for ecological assessments. Metal-based nanoparticles (NPs) can cause toxicity to terrestrial plants; however, there is little understanding of plant defense mechanisms that may counteract nanotoxicity. The occurrence of oxidative pressure is one of the major biochemical alterations following nanoparticle exposure, and it changes the balance between cell function and antioxidative defense mechanisms. Biochemical aspects generally cause the production of excess reactive oxygen species (ROS), disturbing membrane transport mechanisms, oxidative harm to the cell membrane, and DNA degradation. Globally plants had developed the antioxidant mechanism which tends to eliminate the access manufacture of ROS i.e.  $H_2O_2$ , OH<sup> $-$ </sup> and O<sub>2</sub> free radicals. Improved levels of antioxidative enzymes, for instance, superoxide dismutase (SOD), catalase (CAT), and peroxidase (POX), are able to support plant cells in lightening the oxidative stress induced by different nanostructures. As the vital signals resolving defense gene establishment, ROS are principally drawn in the initiation of plant disease resistance responses. Further reviews are still needed to understand plant defense mechanism against the potential hazards of nanomaterials.

#### **Keywords**

Nanomaterials • Plant defense mechanism • Cerium oxide • Chitosan • Silicon

R. Prasad ( $\boxtimes$ ) • N. Gupta • M. Kumar • V. Kumar

#### S. Wang

K.A. Abd-Elsalam Plant Pathology Research Institute, Agricultural Research Centre, Giza, Egypt

© Springer Nature Singapore Pte Ltd. 2017 253

Amity Institute of Microbial Technology, Department of Microbial Technology, Amity University, Noida, Uttar Pradesh 201313, India e-mail: [rprasad@amity.edu](mailto:rprasad@amity.edu); [rpjnu2001@gmail.com](mailto:rpjnu2001@gmail.com)

School of Environmental Science and Engineering, Sun Yat-Sen University, Guangzhou 510006, China

R. Prasad et al. (eds.), *Nanotechnology*, DOI 10.1007/978-981-10-4678-0\_14

#### **14.1 Introduction**

Nanomaterials are particles having a minimum of one dimension smaller than 100 nm. These particles are of great interest because they can bridge the gap among bulk materials and atomic molecular makeup. This is incredibly interesting from scientific point of view, because as it gets smaller, it starts changing its properties (Kothandapani and Mishra [2013\)](#page-12-0). Nanoparticles such as zinc oxide, titanium dioxide have ability to block sun rays and therefore used in preparation of sun block creams and lotions. The use of the word "nano" allows researchers to draw attention to the facts regarding material structures, design, and optimized use of vague properties and behaviors by length from  $10^{-7}$  to  $10^{-9}$  m (Ozimek et al. [2010\)](#page-13-0). The potential advantages of nanomaterials have been recognized by many industries and many commercial products are manufactured such as food, aerospace, pharmaceutical, microelectronics and cosmetic industries (Saboktakin [2012](#page-14-0)). Progresses in these commercial enterprises are propelled by basic and functional research in physics, chemistry, biology, engineering, and material sciences. Achievements and discoveries of nanosciences in food and linked industries are restricted. The structural orientation of compound at nanoscale is significantly dissimilar to the macroscopic counterparts with respect to physical, chemical and biological properties. Nanomaterial research is presently a part of passionate scientific significance due to the diversity of promising application in biomedical, optical, and electronic fields (Prasad et al. [2014\)](#page-13-1). The national nanoscience program has led to liberal public grant for nanoscience research in the USA (Suganeswari et al. [2011\)](#page-15-0). Numerous nanoparticles are manufactured possessing applications in designing and development of optical devices, sensor technology, catalyst, bactericide, electronics, biological labeling, treatment of cancer, and many more (Prasad et al. [2016,](#page-13-2) [2017\)](#page-14-1). In previous decade, application of nanomaterials has been extensively increased, and high demands lead to the bulk production of the nanomaterials. Classically nanomaterials are produced by physical and chemical methods, as these methods are very expensive, poisonous, and non-eco-friendly. In current scenario, scientists are looking for the alternative methods, i.e., biological methods which are low cost, nontoxic, and eco-friendly (Prasad [2014;](#page-13-3) Prasad et al. [2016](#page-13-2)).

NPs are source for various biological and chemical effects on terrestrial plants. (Du et al. [2016\)](#page-11-0). Numerous studies have demonstrated the metal nanoparticle's phytotoxicity caused by the manufacture of reactive oxygen species (ROS), which subsequently results in oxidative stress, lipid peroxidation, and protein and DNA damage in plants (Arruda et al. [2015;](#page-11-1) Ma et al. [2015a](#page-13-4); Tripathi et al. [2017a,](#page-16-0) [b](#page-16-1); Singh et al. [2017a](#page-14-2), [b](#page-15-1)).

Plant cells cannot move so each cell is needed to be capable of defending themselves from the attack of stress and pathogens. Only proteins are involved in plant defense responses and proper cell functioning. Plants had evolved the two types of well defense mechanism. The first line of defense takes place when plant cells sense the presence of herbivore (by detecting general characteristics like flagella of bacteria or the chitin in fungi cell walls) and alert nearby cells by secreting certain chemical molecules that alert other surrounding cells to amplify their defense reaction (Freeman and Beattie [2008\)](#page-12-1). For example, in response to harmful pathogens or invaders, the alerted plant cells may secrete certain molecules that build extra walls for protection. Pathogens evolved and developed the mechanism to tackle the plant first line of defense, in response plant evolved and developed second line of defense. The second line of defense protects the plant from invaders. There are diverse indicators that help to indicate which type of defense must be activated in plant in response to what type of pathogen. By analyzing these signs and the genome of plants, scientists can find out which parts of the plant genome and which proteins are implemented in defense system. The example of the activation of secondary defense response is hypersensitive response (HR). Plant cells align around the pathogen attack site and kill themselves to restrict pathogen from dispersion throughout the plant. This inhibits pathogen uptake of water and nutrients from plants.

#### **14.2 Nanoparticles Exhibiting Plant Defense Mechanisms**

Nanoparticles are the interesting topic for research because their property at nanoscale is different as compared to its normal size. Nanomaterials have been used in crop growing to improve seed germination and plant development and to guard crops from biotic stresses, i.e., herbivore (Khodakovskaya et al. [2009](#page-12-2)). However, the unique properties of NPs on living organisms in the ecosystem may experience oxidative stress induced by NPs (Majumdar et al. [2014](#page-13-5)). Plants can activate various enzymatic and nonenzymatic defense systems (Rico et al. [2015\)](#page-14-3) against stress. One of the interesting properties is amplification of defense response in plants through nanoparticles (Table [14.1](#page-3-0)). Chitosan is known to possess antifungal properties against plant pathogens and induce disease resistance. TiO<sub>2</sub> increases the enzyme activities which decreases the accumulation of reactive oxygen species. Silicon nanoparticles are known to enhance the fungal resistance in maize by expressing higher level of phenolic compound and lower level of stress-responsive enzymes against fungi. A combination of *Pseudomonas fluorescens* and silica NPs in soil increases phenolic action and trims down the stress by the inhibition of responsive enzymes in maize. This elevated level of phenolics is established to induce silica accumulation in leaf epidermal layer, thereby conferring a defensive physical wall as well as induced disease resistance (Rangaraj et al. [2014\)](#page-14-4). Copper oxide nanoparticles accumulate in the plant cells and increase the significant levels of superoxide dismutase, catalase, and lipid peroxidase.

A large number of reports have studied activation of antioxidative enzymes in response to nanomaterial exposure (Tripathi et al. [2017a](#page-16-0), [c\)](#page-16-2). Antioxidant enzymes can be activated by a variety of nanomaterials i.e.  $nCeO<sub>2</sub>$ ,  $nFe<sub>3</sub>O<sub>4</sub>$ , and  $nCo<sub>3</sub>O<sub>4</sub>$  can induce CAT; *n*CeO<sub>2</sub>, *n*Fe<sub>3</sub>O<sub>4</sub>, *n*Co<sub>3</sub>O<sub>4</sub>, *n*MnO<sub>2</sub>, *n*CuO, and *n*Au can induce GPX; and *n*CeO<sub>2</sub>, *n*Pt, and fullerene can induce SOD (Tripathi et al. [2016a\)](#page-15-2). Antioxidant defense mechanism of plants employs both enzymatic agents such as superoxide dismutase (SOD), catalase (CAT), ascorbate peroxidase (APX), guaiacol peroxidase (GPX), dehydroascorbatereductase (DHAR), and glutathione reductase (GR)

S. no	Nanoparticles	Mode of action	References
$\mathbf{1}$	Chitosan	Upregulation of defense-related genes including that of several antioxidant enzymes as well as Elevation of the levels of total phenolics and NO signaling molecule	Chandra et al. (2015)
$\overline{2}$	TiO <sub>2</sub>	Increased activity of superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD) and decreased accumulation of reactive oxygen free radicals	Hong et al. $(2005)$
3	Multi-walled carbon nanotubes (MWCNTs)	Activation of ROS defense response cascade, which is sufficient to prevent microbial pathogens from completing their life cycle Generation of ROS such as super peroxides and $H_2O_2$	Tan et al. $(2009)$ and Begum and Fugetsu (2012)
$\overline{4}$	Silicon	Enhanced fungal resistance in maize	Rangaraj et al. (2014)
5	Copper oxide	Increases levels of SOD, CAT, and lipid peroxidase	Nekrasova et al. 2011
6	Cerium oxide	$CeO2$ concentration-dependent induction of lipid peroxidation and photosynthetic stress in rice seedlings (modifications of antioxidant defense system)	Majumdar et al. (2014)
7	Zinc oxide	Increased GSH levels and CAT activity	Zhao et al. (2013)

<span id="page-3-0"></span>**Table 14.1** Nanoparticles and its mode of action

and nonenzymatic antioxidants such as ascorbate, glutathione, thiols, phenolics, etc. (Singh et al. [2015;](#page-14-5) Rico et al. [2015](#page-14-3)). ROS are fairly manufactured as byproducts of metabolic pathways in chloroplasts and are also accountable for chlorophyll degradation (Melegari et al. [2013;](#page-13-6) Rico et al. [2015;](#page-14-3) Ma et al. [2015a;](#page-13-4) Singh et al. [2017a](#page-14-2), [b\)](#page-15-1). However, disorder in plant photosynthetic activity by NPs can generate ROS and stimulate the plants' defense pathway to fight oxidative stress damage (Shweta et al. [2016](#page-14-6)). Enzymes (such as SOD, CAT, POD (peroxidase), GPX and APX, thiol contents (GSSG or GSH), and malondialdehyde (MDA) content) are commonly changed as a result of the fluctuation of ROS concentration (Arif et al. [2016](#page-11-2)).

Multi-walled carbon nanotubes (MWCNTs) activate ROS defense response cascade, which prevents microbial pathogens from completing their life cycle. As compared to other metals and polymers, a very detailed study is done on the cerium oxide nanoparticles, which shows promising ROS scavenging enzymes mimicking activities. This property elevates the defense system in plants.

#### **14.2.1 Chitosan Nanoparticles**

Chitosan is a linear polymer composed of arbitrarily scattered D-glucosamine (deacetylated unit) and *N*-acetyl-p-glucosamine (acetylated unit) by the means of  $β-(1-4)$ -linkage. They are synthesized by treating the chitin shells of shrimp and other crustaceans with an alkaline solution (i.e., sodium hydroxide). Many naturally occurring polysaccharides are acidic in nature, but chitosan is the basic polymer occurring naturally.

Chitosan is widely used in cosmetics and substance-based applications. However, in current times biomedicine and agriculture have shown a rising interest in chitosan polymer as a therapeutic agent. It has been reported in the plant system that chitosan has the ability to induce multifaceted disease resistance (Hadrami et al. [2010](#page-12-4)). This naturally occurring biopolymer is widely studied for its significant properties like biocompatibility, biodegradability, nontoxicity, and antimicrobial activity, thus accepting its use as an initiator molecule for diverse host-pathogen interaction studies and analysis (Saharan et al. [2015](#page-14-7); Prasad et al. [2017](#page-14-1)). These specific properties of chitosan can be further improved by using it in the structure of nanoparticles. In this structure it possesses quite different biological activities with distorted physicochemical features, i.e., size, surface area, cationic nature, etc. Its exclusive biocompatibility, biodegradability, and less poisoning nature make chitosan nanoparticles (CNP) a successful nano-transportation method than its close counterparts. However, the CNP are not only more stable and less poisonous, but also it does not require any complicated methods; it only needs use of uncomplicated preparative methods which make them a diverse and user-pleasant drug delivery mediator (Nagpal et al. [2010\)](#page-13-8). Apart from biomedical implementations, CNP are only reported to have antifungal properties in response to different plant pathogens (Saharan et al. [2013](#page-14-8)). Nanoparticles by themselves can deal with cell walls and membranes more efficiently as compared to the foundation molecules from which they are prepared. Natural defense mechanism of plants relies upon early detection of pathogens. During evolution, plants have developed diverse mechanism to fight different evolving pathogens. The induction of natural defense mechanism involves overexpression of different defensive genes and enzymes, amplified deposition of phenolic compounds, cell wall synthesis, etc. Plants treated with different biological elicitor molecules have shown to provoke such innate immune response by mimicking variety of pathogens (McCann et al. [2012\)](#page-13-9). As an exogenous elicitor, chitosan can stimulate resistance in plant host by increasing some defense-related enzyme activities, such as PAL, POD, CAT, SOD, and polyphenol oxidase (PPO) activities (Xing et al. [2015\)](#page-16-4). Recently, Chandra et al. ([2015\)](#page-11-3) have reported that accumulation of CNP increases the plant defense by increasing the levels of SOD and CAT. CNP binds extracellular around the cell wall of the leaves. One of the most important signaling molecules is NO, which is also coupled with many physiological processes involving initiation of defense system in plants. Plants treated with CNP showed increased levels of NO, as compared to plants not treated with CNP (Raho et al. [2011](#page-14-9); Malerba et al. [2012](#page-13-10)). CNP-treated sets resulted in upregulation of PAL activity leading to the higher level of phenolic compound accumulation. Phenylalanine ammonia lyase

(PAL), cinnamic acid 4-hydroxylase (C4H), and flavanone 3-hydroxylase (F3H) are the set of genes involved in flavonoid biosynthesis. PAL and C4H are important control points of phenylpropanoid biological synthesis. F3H is involved in flavonoid synthesis pathway in biological system yielding diverse family of flavonoid compounds possessing many types of activities, i.e., disease resistance. Higher accumulation of flavonoids like gallic acid (GA), epicatechin (EC), epigallocatechin (EGC), and caffeine was seen when sets were treated with CNP. These accumulated phytochemicals assist in adaptation to various environmental circumstances and provide resistance against pathogen by performing as feeding deterrents. In the presence of NADPH, anthocyanidin reductase (ANR) uses anthocyanidins as substrates to synthesize EC. EC ultimately changed to proanthocyanidins, which is commonly dispersed as plant defense compounds possessing intense toxicity toward pathogens. High levels of flavonoid deposition are an indication of improved resistance to plants. In CNP-treated plants higher expression of SOD and CAT was observed resulting in increased level of these enzymes. SOD and CAT are the essential antioxidant enzymes implicated in ROS scavenging system (Chandra et al. [2015\)](#page-11-3). Polyphenol oxidase produce lignin from phenolic substances in angiosperm, it contributes in the thickening of cell wall structure and restricting pathogen entry (Li and Zhu [2013\)](#page-12-5). ROS,  $Ca^{2+}$ , nitric oxide (NO), ethylene (ET), jasmonic acid (JA), salicylic acid (SA), and abscisic acid (ABA) all involved in chitosan-mediated signaling pathway (Xing et al. [2015](#page-16-4)). Nano-plant self-defense mechanism of the activated nano-chitosan through different modes of action such as pathogenesis involved proteins, defense-associated enzymes, and secondary metabolite deposition, in addition to the complicated signal transduction network (Fig. [14.1](#page-6-0)).

#### **14.2.2 TiO, Nanoparticles**

The activity of  $TiO<sub>2</sub>$  nanoparticles on the chloroplast aging of spinach in response to illumination was studied by Hong et al. [\(2005](#page-12-3)). Results represented that whenever chloroplasts were treated for 1, 5, and 10 min with 500 micromol/cm<sup>2</sup>/min light intensity, the rate of oxygen liberation was speedily accelerated; when the chloroplasts were illuminated for 20, 30, and 40 min with 500 micromol/cm<sup>2</sup>/min light intensity, the rate of oxygen liberation was statistically reduced. When spinach was treated with  $0.25\%$  TiO<sub>2</sub> nanoparticles, the rate of oxygen liberation of chloroplasts in various illumination times (1, 5, 10, 20, 30, and 40 min) was more as compared to control, and when illumination time was exceeded by 10 min, the reduction of the liberated oxygen rate was less as compared to control. Hong et al. ([2005\)](#page-12-3) concluded that TiO2 nanoparticle treatment might defend chloroplasts aging for extended-time illumination. This mechanism represents that  $TiO<sub>2</sub>$  nanoparticle treatment significantly increases the defense properties of POD, SOD, and CAT. Decrease deposition of ROS and the level of malondialdehyde (MDA) maintain steadiness of membrane structure of chloroplast treated with luminance (Hong et al. [2005\)](#page-12-3).CAT activity was increased (250–750 mg/kg) but was decreased in ascorbate peroxidase (APX) (500 mg/kg) when cucumber plants were treated with nano-TiO<sub>2</sub> (Servin

<span id="page-6-0"></span>

et al. [2013\)](#page-14-10). The effect of nano-TiO<sub>2</sub> sprayed on pinto bean (*Phaseolus vulgaris*) was significant on activities of SOD, CAT, POD,MDA, and 8-deoxy-2-hydroxyguanosine (8-OHDG) content (Ebrahimi et al. [2016](#page-12-6)).

#### **14.2.3 Multi-walled Carbon Nanotubes (MWCNTs) Nanoparticles**

Multi-walled carbon nanotubes are diversely used in nanoscience in spite of concerns regarding probable poisonous effects. To conclude whether MWCNTs are toxic to *Oryza sativa* were treated with MWCNTs (Tan and Fugetsu [2009\)](#page-15-3). Rice cells reacted with MWCNTs to develop aggregates that were analyzed using compound and scanning electron microscopy. Cell density gradually decreased with increased MWCNT concentration, probably representing a self-defense response. Thus, MWCNTs interact directly with rice cells and might have a damaging effect on rice growth and development. This property, although, was stronger as compared to carbon blacks; the rice cells survived the MWCNTs via self-defense mechanism (Tan and Fugetsu 2007). Tan et al. ([2009\)](#page-15-3) showed that when rice seedlings were exposed with MWCNTs, the ROS levels significantly increased and the cell viability decreased. This is because these nanotubes make contact with the cell walls and undergo ROS defense response cascade, which is ample to avoid microbial pathogens from finishing their life cycle (Smirnova et al. [2011](#page-15-4)). Moreover, Lin and Xing ([2007](#page-12-7)) also observed apoptosis in cells of lettuce exposed to multiwall carbon nanotube.

#### **14.2.4 Silicon Nanoparticles**

Silicon is regarded as one of the most beneficial elements for the growth and development of plants which is available as second most abundant element of the Earth's crust (Epstein [1999](#page-12-8); Tripathi et al. [2012a](#page-15-5), [b](#page-15-6)). It is accumulated by plant roots in the form of monosilicic acid and deposited in and between the plant cells which is called as phytoliths (Tripathi et al. [2012c,](#page-15-7) [d](#page-15-8), [2013](#page-15-9), [2014](#page-15-10), [2016b](#page-16-5)). In the form of phytolith deposition in plant cells, silicon provides the mechanical strength to plants from various biotic and abiotic stresses (Ma [2004](#page-13-11); Tripathi et al. [2014](#page-15-10), [2015b,](#page-15-11) [2016c](#page-16-5), [d](#page-16-6), [2017d\)](#page-16-7). Thus it will be more interesting and matter of great curiosity for the agricultural scientists to observe the behavior of silicon in the form of nanoparticles for the plants. In this connection in a study by Suriyaprabha et al. ([2014\)](#page-15-12), nanosilica treatment is screened for resistance in maize in response to plant pathogens such as *Fusarium oxysporum* and *Aspergillus niger* and comparative analysis done with bulk silica activity. The resistance is measured for pathogenicity index and expression of plant reactive compounds such as total phenolics, phenylalanine ammonia lyase, peroxidase, and polyphenol oxidase. The results represented higher expression level of phenolic compounds (2056 and 743 mg/ml) and a lower expression level of stress-responsive enzymes in response to both the fungi in nanosilicatreated plants. Maize expresses high resistance to *Aspergillus* spp., as compared to *Fusarium* spp. These results represent significantly elevated resistance in maize when treated with nanosilica as compared with bulk, especially at 10 and 15 kg/ha. However, hydrophobic potential and silica deposition quantity of nanosilica-treated maize (86.18° and 19.14%) are higher than bulk silica treatment. Hence, silica nanoparticles might be used as another potent antifungal agent against plant pathogens (Suriyaprabha et al. [2014\)](#page-15-12). In addition Tripathi et al. [\(2017e](#page-16-8)) have reported the significant alleviative nature of silicon nanoparticles against the UV-B stress in wheat seedlings. Similarly, silicon nanoparticles have been also found to detoxify the arsenic and chromium stress in wheat and *Pisum sativum* seedlings, respectively (Tripathi et al. [2015a,](#page-15-13) [b,](#page-15-11) [2016a](#page-15-2), [b](#page-15-14), [c,](#page-16-5) [d](#page-16-6), [e](#page-16-9)).

#### **14.2.5 Copper Oxide Nanoparticles**

Copper oxide nanoparticles have brownish-black powder appearance. They are reduced to metal copper when treated with hydrogen or carbon monoxide in the presence of high temperature. They are harmful to humans and hazardous to ecosystem with detrimental consequence on aquatic life. CuO NPs are one of the most important and regularly used engineered oxide NPs with major industrial, medical, and environmental applications (Adhikari et al. [2012;](#page-11-5) Yadav et al. [2017](#page-16-10)). Nanoparticles are more vigorously deposited by plants. Nekrasova et al. [\(2011](#page-13-7)) reported that CAT and SOD activity are increased by the factor of 1.5–2.0 and lipid peroxidation activated when *Elodea densa* are exposed to copper oxide nanoparticles. In rice plantlets, nano-CuO treatment led to an amplified activity of antioxidant enzymes and increased MDA concentration (Shaw and Hossain [2013\)](#page-14-11). Treatment with *n*CuO nanoparticles results in considerable oxidative stress i.e. higher ROS and MDA content with elevated actions of some anto-oxidative enzymes in rice (Da Costa and Sharma [2016](#page-11-6); Shaw and Hossain [2013](#page-14-11); Wang et al. [2015\)](#page-16-11), wheat (Dimkpa et al. [2012](#page-11-7)), soybean (Nair and Chung [2014a\)](#page-13-12), *Elodea densa* (Nekrasova et al. [2011\)](#page-13-7), and *Arabidopsis thaliana* (Nair and Chung [2014b\)](#page-13-13). It lead reduced CAT activity in alfalfa (Hong et al. [2015\)](#page-12-9) and inhibited APX in Indian mustard (Nair and Chung [2015\)](#page-13-14). A related assay on nano-CuO-mediated photosynthetic activity and antioxidative defense system in *Hordeum vulgare* revealed obstruction in root and shoot development with reduced photosynthetic performance index (Shaw et al. [2014](#page-14-12)).

#### **14.2.6 Cerium Oxide Nanoparticles**

Cerium has gained much attention of researchers from the field of physics, chemistry, metal science, and biology because it belongs to lanthanide group with 4f electrons. Formation of cerium oxide nanoparticles involves reaction between cerium and oxygen. This nanoparticle structure exhibits the fluorite crystalline structure that comes forward as charming material (Conesa [1995](#page-11-8)) variety of applications in engineering and biological arena involves effective incorporation of cerium oxide nanoparticles (Stambouli and Traversa [2002](#page-15-15)), high-temperature oxidation defense materials (Patil et al. [2002\)](#page-13-15), catalytic materials (Trovarelli [1996](#page-16-12); Kaspar et al. [1999\)](#page-12-10), solar cells (Corma et al. [2004\)](#page-11-9), and potential pharmacological agents (Celardo et al. [2011\)](#page-11-10). CeONPs exhibit unique structure and atomic properties which result in its incorporation in the field of catalysis and stem cell research. In current years, CeONP has come under extreme study as a catalyst, as electronic, and as structural promoters of various catalytic reactions (Trovarelli [1996](#page-16-12)). In industries, it is applied as an active component more extensively in courses, i.e., three-way catalyst (Kaspar et al. [1999](#page-12-10)) for vehicle exhaust-gas treatments, oxidative union of methane, and water-gas shift reaction. Lately, CeONP reported to contain multienzyme including superoxide oxidase, catalase, and oxidase, mimicking properties. It has come into view as an attractive and profitable material in biological sciences such as in bioanalysis (Asati et al. [2009,](#page-11-11) [2011;](#page-11-12) Li et al. [2011](#page-12-11); Ornatska et al. [2011;](#page-13-16) Kaittanis et al. [2012](#page-12-12); Lin et al. [2012\)](#page-13-17), biomedicine (Celardo et al. [2011](#page-11-10)), drug delivery (Xu et al. [2013](#page-16-13); Li et al. [2013a](#page-12-13)), and bioscaffolding (Karakoti et al. [2010](#page-12-14); Mandoli et al. [2010\)](#page-13-18). Peroxide offers a source of hydroxyl radicals, which play a key role in oxidative damage. Das et al. ([2007\)](#page-11-13) concluded that the defensive effect of CeONP on the spinal cord implicates its free radical scavenging property (Fig.  $14.2$ ). In other reports, nano-CeO<sub>2</sub> increased H2O2 generation in corn (Zhao et al. [2012](#page-16-14)) and *Brassica rapa* (Ma et al. [2015b\)](#page-13-19) but led to lower  $H_2O_2$  in rice (Rico et al. [2013b,](#page-14-13) [c\)](#page-14-14). Exposure of sprouting rice seedlings to extremely concentrated CeONPs has disturbed free thiol levels, ascorbate, and enzyme activities leading to greater photosynthetic pressure and membrane injury in shoots (Rico et al. [2013a](#page-14-15)). Analysis of ROS scavenger activity indicated that behavior of SOD, CAT, APX, and POD was significantly elevated upon exposure to  $CeO<sub>2</sub>$  NPs, while these elevations were only evident for SOD and POD

<span id="page-9-0"></span>

**Fig. 14.2** Schematic detailing the proposed mechanism of the CeONP free radical scavenging property and autocatalytic behavior (Das et al. [\(2007](#page-11-13)) Copyright, Elsevier)

activities in the  $In_2O_3$  NP treatments. Furthermore, the behavior of glutathione S-transferase (GST) and glutathione reductase (GR) was increased by approximately 15% and 51% by 1000 mg L<sup>-1</sup> CeO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> reaction. Moreover, activities of phenylalanine ammonia lyase (PAL) and polyphenol oxidase (PPO) were significantly induced in response to both types of NP (Ma et al. [2016](#page-13-20)).

The transportation mechanism of  $CeO<sub>2</sub>$  nanoparticles in plants and their effect on cellular homeostasis depending upon their exposure duration are not well understood. In a recent study, Majumdar et al. $(2014)$  $(2014)$  reported that kidney-shaped bean plants when treated with suspensions of  $\sim$  8 ± 1 nm nCeO<sub>2</sub> (62.5–500 mg/L) for fortnight in hydroponic environment, the principal indicators of stress, i.e., lipid peroxidation, antioxidant enzyme activities, total soluble protein, and chlorophyll contents, showed certain. Cerium in tissues was localized and studied using scanning electron microscopy and synchrotron μ-XRF mapping. The chemical structures were identified using μ-XANES. In the root epidermis, cerium was shown to stay as nCeO<sub>2</sub>; however, a small fraction (12%) was biotransformed to Ce(III) compound. Cerium reaches the root vascular tissues and translocates to upper parts of plant with time. Upon extended exposure to 500 mg nCeO<sub>2</sub>/L, the root's antioxidant activity was extensively reduced, side by side elevating the solubilization of root protein by 204%. Guaiacol peroxidase is one of the most important ROS scavenging enzymes found in plants (antioxidants response to salinity and ameliorating its effect by *Nigella sativa*). The leaf's guaiacol peroxidase activity was improved with  $nCeO<sub>2</sub>$  introduction in order to sustain cellular homeostasis.

 $CeO<sub>2</sub>$  possesses various activities that make it most reliable metal nanoparticle to enhance the plant defense system. Few of the activities were documented: superoxide dismutase mimetic activity, catalase mimetic activity, nitric oxide radical scavenging, hydroxyl radical scavenging, peroxidase mimetic activity, oxidase mimetic activity, and phosphatase mimetic activity (Das et al. [2013](#page-11-14); Nelson et al. [2016](#page-13-21)).

Recently Kuchma et al. [\(2010](#page-12-15)) concluded that molecules biologically related with phosphate ester (i.e., not DNA) can be hydrolyzed by CeONPs. Fascinatingly, they discovered dephosphorylation activity of CeONP depending on the presence of  $Ce^{3+}$  sites and restricted when  $Ce^{3+}$  is changed into  $Ce^{4+}$ . This opposes the thinning of Ce4+-mediated hydrolysis by Qian and colleagues (Tan et al. [2008\)](#page-15-16). To understand the pathway, further research is required.

#### **14.2.7 Zinc Oxide Nanoparticles**

Nano-Zn increased GSH levels and CAT activity in buckwheat leaves (Lee et al. [2013\)](#page-12-16) (1-1000mg/ml) but showed no effect on APX activity (100–800 mg/kg) and reduced CAT activity (at 400 mg/kg) in corn leaves grown in soil amended with alginate (Zhao et al. [2013](#page-16-3)). Kim et al. [\(2012](#page-12-17)) noticed high activity for SOD, POD, and CAT when treated by nano-CuO and nano-ZnO in cucumber plants. ZnO NP exposure to the plants significantly promoted the growth rate, biomass, photosynthetic pigment levels, and protein content, while MDA production declined compared to the control. Interestingly, the ZnO NPs increased the action of antioxidant defense enzymes and upregulated the production level of SOD and POX isoenzymes in *Gossypium hirsutum* plants (Priyanka and Venkatachalam [2016](#page-14-16)). Production of ROS, RNS (reactive nitrogen species), and peroxide upon treatment with ZnO and Ag engineered NPs on the *Spirodela punctuta* shows the potential toxicity of Ag and ZnO nanoparticles principally grounded by the particulates and ionic forms (Thwala et al. [2013](#page-15-17)). SOD enzyme activity was increased after ZnO NP exposure, showing an amplification of the ROS scavenging process in *Spirodela polyrhiza* (Hu et al. [2013\)](#page-12-18). The CAT and POX are notable antioxidant defense enzymes implicated in the detoxification of peroxide by changing free radicals to water and oxygen (Ma et al. [2015a,](#page-13-4) [b](#page-13-19)).

#### **14.2.8 Plant Induced Resistance**

ROS not only restrict pathogen entrance but also play an important role in activating local and systemic defense systems such as the stimulation of pathogenesisassociated protein genes (Henry et al. [2013\)](#page-12-19). The plant hormones salicylic acid, jasmonic acid, and ethylene participate significant roles in defense reactions as signaling molecules (Robert-Seilaniantz et al.  $2011$ ). The speedy production of  $O<sub>2</sub>$  or phenoxyl radicals in tomato roots treated with MgO NPs may play a related role in the resistance response of tomatoes against *Ralstonia solanacearum* (Imada et al. [2016\)](#page-12-20). Chitosan extensively elevates polyphenol oxidase activity in rice plantlets followed by inoculation of two rice pathogens (*Xanthomonas oryzae* pv. o*ryzae* and *X. oryzae* pv. *oryzicola*) (Li et al. [2013b\)](#page-12-21). Silver and ZnO NP treatment lead to increase in contents of free radicals, together with ROS, reactive nitrogen species, and hydrogen peroxide in duckweed (Thwala et al. [2013\)](#page-15-17). NPs discovered to induce oxidative stress and altered gene expression in plants (Wang et al. [2013](#page-16-15)).

### **14.3 Conclusion**

The consequence of nanoparticles on gene expression with plant response to main supplies of environmental pressure leads the way to remediate the result of these possible harmful compounds through hormonal priming. Numerous studies are done dealing with plant response to the precise NP stress presenting differential mechanism involved in ROS detoxification, oxidation reduction, hormonal pathways and stress signaling. The mode of action of how NPs act on plant immunity maintenance has not been clarified. It is assumed that the mechanisms of NPs are possibly more complex than explained above, linking to a long way of actions, which need to further research and studies.

#### **References**

- <span id="page-11-5"></span>Adhikari T, Kundu S, Biswas AK, Tarafdar JC, Rao AS (2012) Effect of copper oxide nanoparticle on seed germination of selected crops. J Agric Sci Technol A2:815–823
- <span id="page-11-2"></span>Arif N, Yadav V, Singh S, Kushwaha BK, Singh S, Tripathi DK, Vishwakarma K, Sharma S, Dubey NK, Chauhan DK (2016) Assessment of antioxidant potential of plants in response to heavy metals. In: Plant responses to xenobiotics. Springer Singapore, Singapore, pp 97–125
- <span id="page-11-1"></span>Arruda SCC, Silva ALD, Galazzi RM, Azevedo RA, Arruda MAZ (2015) Nanoparticles applied to plant science: a review. Talanta 131:693–705
- <span id="page-11-11"></span>Asati A, Santra S, Kaittanis C, Nath S, Perez JM (2009) Oxidase like activity of polymer coated cerium oxide nanoparticles. Angew Chem Int Ed 48:2308–2312
- <span id="page-11-12"></span>Asati A, Kaittanis C, Santra S, Perez JM (2011) pH-tunable oxidase like activity of cerium oxide nanoparticles achieving sensitive fluorigenic detection of cancer biomarkers at neutral pH. Anal Chem 83:2547–2553
- <span id="page-11-4"></span>Begum P, Fugetsu B (2012) Phytotoxicity of multi-walled carbon nanotubes on red spinach (*Amaranthus tricolor* L.) and the role of ascorbic acid as an antioxidant. J Hazard Mater 243:212–222
- <span id="page-11-10"></span>Celardo I, Pedersen JZ, Traversa E, Ghibelli L (2011) Pharmacological potential of cerium oxide nanoparticles. Nanoscale 3:1411–1420
- <span id="page-11-3"></span>Chandra S, Chakraborty N, Dasgupta A, Sarkar J, Panda K, Acharya K (2015) Chitosan nanoparticles: a positive modulator of innate immune responses in plants. Sci Rep 5:Article 15195
- <span id="page-11-8"></span>Conesa JC (1995) Computer modeling of surfaces and defects on cerium dioxide. Surf Sci 339:337–352
- <span id="page-11-9"></span>Corma A, Atienzar P, Garcia H, Chane Ching JY (2004) Hierarchically mesostructured doped  $CeO<sub>2</sub>$  with potential for solar cell use. Nat Mater 3:394–397
- <span id="page-11-6"></span>Da Costa MVJ, Sharma PK (2016) Effect of copper oxide nanoparticles on growth, morphology, photosynthesis, and antioxidant response in *Oryza sativa*. Photosynthetica 54(1):110–119
- <span id="page-11-13"></span>Das M, Patil S, Bhargava N, Kang JF, Riedel LM, Seal S, Hickman JJ (2007) Autocatalytic ceria nanoparticles offer neuroprotection to adult rat spinal cord neurons. Biomaterials 28:1918–1925
- <span id="page-11-14"></span>Das S, Dowding JM, Klump KE, McGinnis JF, Self W, Seal S (2013) Cerium oxide nanoparticles: applications and prospects in nanomedicine. Nanomedicine 8(9):1483–1508. doi:[10.2217/](http://dx.doi.org/10.2217/nnm.13.133) [nnm.13.133](http://dx.doi.org/10.2217/nnm.13.133)
- <span id="page-11-7"></span>Dimkpa CO, McLean JE, Latta DE, Manangon E, Britt DW, Johnson WP, Boyanov MI, Anderson AJ (2012) CuO and ZnO nanoparticles: phytotoxicity, metal speciation, and induction of oxidative stress in sand-grown wheat. J Nanopart Res 14:1–15
- <span id="page-11-0"></span>Du W, Tan W, Peralta-Videa JR, Gardea-Torresdey JL, Ji R, Yin Y, Guo H (2016) Interaction of metal oxide nanoparticles with higher terrestrial plants: physiologic al and biochemical aspects. Plant Physiol Biochem 110:210–225
- <span id="page-12-6"></span>Ebrahimi A, Galavi M, Ramroudi M, Moaveni P (2016) Effect of TiO<sub>2</sub> nanoparticles on antioxidant enzymes activity and biochemical biomarkers in Pinto Bean (*Phaseolus vulgaris* L.) J Mol Biol Res 6:58–66
- <span id="page-12-4"></span>El Hadrami A, Adam LR, El Hadrami I, Daayf F (2010) Chitosan in plant protection. Mar Drugs 8:968–987
- <span id="page-12-8"></span>Epstein E (1999) Silicon. Annu Rev Plant Biol 50(1):641–664
- <span id="page-12-1"></span>Freeman BC, Beattie GA (2008) An overview of plant defenses against pathogens and herbivores. Plant Health Instructor. doi[:10.1094/PHI-I-2008-0226-01](http://dx.doi.org/10.1094/PHI-I-2008-0226-01)
- <span id="page-12-19"></span>Henry E, Yadeta KA, Coaker G (2013) Recognition of bacterial plant pathogens: local, systemic and transgene rational immunity. New Phytol 199:908–915
- <span id="page-12-3"></span>Hong F, Yang F, Liu C, Gao Q, Wan Z, Gu F, Wu C, Ma Z, Zhou J, Yang P (2005) Influences of nano-TiO2 on the chloroplast aging of spinach under light. Biol Trace Elem Res 104(3):249–260
- <span id="page-12-9"></span>Hong J, Rico CM, Zhao L, Adeleye AS, Keller AA, Peralta-Videa JR, GardeaTorresdey JL (2015) Toxic effects of copper-based nanoparticles or compounds to lettuce (*Lactuca sativa*) and alfalfa (*Medicago sativa*). Environ Sci Process Impacts 17:177–185
- <span id="page-12-18"></span>Hu C, Liu Y, Li X, Li M (2013) Biochemical responses of duckweed (*Spirodela polyrhiza*) to zinc oxide nanoparticles. Arch Environ Contam Toxicol 64:643–651
- <span id="page-12-20"></span>Imada K, Sakai S, Kajihara H, Tanaka S, Ito S (2016) Magnesium oxide nanoparticles induce systemic resistance in tomato against bacterial wilt disease. Plant Pathol 65:551–560
- <span id="page-12-12"></span>Kaittanis C, Santra S, Asati A, Perez JM (2012) A cerium oxide nanoparticles based device for the detection of chronic inflammation via optical and magnetic resonance imaging. Nanoscale 4:2117–2123
- <span id="page-12-14"></span>Karakoti AS, Tsigkou O, Yue S, Lee PD, Stevens MM, Jones JR, Seal S (2010) Rare earth oxides as nanoadditives in 3D nanocomposite scaffolds for bone regeneration. J Mater Chem 20:8912–8919
- <span id="page-12-10"></span>Kaspar J, Fornasiero P, Graziani M (1999) Use of  $CeO<sub>2</sub>$  based oxides in the three way catalysis. Catal Today 50:285–298
- <span id="page-12-2"></span>Khodakovskaya M, Dervishi E, Mahmood M, Xu Y, Li Z, Watanabe F, Biris AS (2009) Carbon nanotubes are able to penetrate plant seed coat and dramatically affect seed germination and plant growth. ACS Nano 3:3221–3227
- <span id="page-12-17"></span>Kim S, Lee S, Lee I (2012) Alteration of phytotoxicity and oxidant stress potential by metal oxide nanoparticles in *Cucumis sativus*. Water Air Soil Pollut 223(5):2799–2806
- <span id="page-12-0"></span>Kothandapani B, Mishra AK (2013) Synthesis of poly (methacrylate) encapsulated magnetite nanoparticles via phosphoric acid anchoring chemistry and its applications towards biomedicine, chapter 3. In: Nanomedicine for drug delivery and therapeutics. Wiley, Hoboken, pp 63–86
- <span id="page-12-15"></span>Kuchma MH, Komanski C, Colon J, Teblum A, Masunov AE, Alvarado B, Babu S, Seal S, Summy J, Baker CH (2010) Phosphate ester hydrolysis of biologically relevant molecules by cerium oxide nanoparticles. Nanomed Nanotechnol 6:738–744
- <span id="page-12-16"></span>Lee S, Kim S, Kim S, Lee I (2013) Assessment of phytotoxicity of ZnO NPs on a medicinal plant, *Fagopyrum esculentum*. Environ Sci Pollut Res 20:848–854
- <span id="page-12-5"></span>Li SJ, Zhu TH (2013) Biochemical response and induced resistance against anthracnose (*Colletotrichum camelliae*) of camellia (*Camellia pitardii*) by chitosan oligosaccharide application. For Pathol 43:67–76. doi[:10.1111/j.1439-0329.2012.00797.x](http://dx.doi.org/10.1111/j.1439-0329.2012.00797.x)
- <span id="page-12-11"></span>Li X, Sun L, Ge A, Guo Y (2011) Enhanced chemiluminescence detection of thrombin based on cerium oxide nanoparticles. Chem Commun 47:947–949
- <span id="page-12-13"></span>Li B, Liu BP, Shan CL, Ibrahim M, Lou YH, Wang YL, Xie GL, Li HY, Sun GC (2013a) Antibacterial activity of two chitosan solutions and their effect on rice bacterial leaf blight and leaf streak. Pest Manag Sci 69:312–320. doi[:10.1002/ps.3399](http://dx.doi.org/10.1002/ps.3399)
- <span id="page-12-21"></span>Li M, Shi P, Xu C, Ren JS, Qu XG (2013b) Cerium oxide caged metal chelator: antiaggregation and antioxidation integrated  $H_2O_2$  responsive controlled drug release for potential Alzheimer's disease treatment. Chem Sci 4:2536–2542
- <span id="page-12-7"></span>Lin D, Xing B (2007) Phytotoxicity of nanoparticles: inhibition of seed germination and root growth. Environ Pollut 150:243–250
- <span id="page-13-17"></span>Lin YH, Xu C, Ren JS, Qu XG (2012) Using thermally regenerable cerium oxide nanoparticles in biocomputing to perform labelfree, resettable, and colorimetric logic operations. Angew Chem Int 51:12579–12583
- <span id="page-13-11"></span>Ma JF (2004) Role of silicon in enhancing the resistance of plants to biotic and abiotic stresses. Soil Sci Plant Nutr 50(1):11–18
- <span id="page-13-4"></span>Ma CX, White JC, Dhankher OP, Xing B (2015a) Metal-based nanotoxicity and detoxification pathways in higher plants. Environ Sci Technol 49(12):7109–7122
- <span id="page-13-19"></span>Ma XM, Wang Q, Rossi L, Zhang WL (2015b) Cerium oxide nanoparticles and bulk Cerium oxide lead to different physiological and biochemical responses in *Brassica rapa*. Environ Sci Technol. <http://dx.doi.org/10.1021/acs.est.5b04111>
- <span id="page-13-20"></span>Ma C, Liu H, Guo H, Musante C, Coskun SH, Nelson BC, White JC, Xing B, Dhankher O-P (2016) Defense mechanisms and nutrient displacement in *Arabidopsis thaliana* upon exposure to  $CeO<sub>2</sub>$  and  $In<sub>2</sub>O<sub>3</sub>$  nanoparticles. Environ Sci Nano 3:1369–1379
- <span id="page-13-5"></span>Majumdar S, Peralta-Videa JR, Bandyopadhyay S, Castillo-Michel H, Hernandez-Viezcas JA, Sahi S, Gardea-Torresdey JL (2014) Exposure of cerium oxide nanoparticles to kidney bean shows disturbance in the plant defense mechanisms. J Hazard Mater 278:279–287
- <span id="page-13-10"></span>Malerba M, Crosti P, Cerana R (2012) Defense/stress responses activated by chitosan in sycamore cultured cells. Protoplasma 249:89–98
- <span id="page-13-18"></span>Mandoli C, Pagliari F, Pagliari S, Forte G, Di Nardo P, Licoccia S, Traversa E (2010) Stem cell aligned growth induced by  $CeO<sub>2</sub>$  nanoparticles in PLGA scaffolds with improved bioactivity for regenerative medicine. Adv Funct Mater 20:1617–1624
- <span id="page-13-9"></span>McCann HC, Nahal H, Thakur S, Guttman DS (2012) Identification of innate immunity elicitors using molecular signatures of natural selection. Proc Natl Acad Sci 109:4215–4220
- <span id="page-13-6"></span>Melegari SP, Perreault F, Costa RHR, Popovic R, Matias WG (2013) Evaluation of toxicity and oxidative stress induced by copper oxide nanoparticles in the green alga *Chlamydomonas reinhardtii*. Aquat Toxicol 142:431–440
- <span id="page-13-8"></span>Nagpal K, Singh SK, Mishra DN (2010) Chitosan nanoparticles: a promising system in novel drug delivery. Chem Pharm Bull (Tokyo) 58:1423–1430
- <span id="page-13-12"></span>Nair PMG, Chung IM (2014a) A mechanistic study on the toxic effect of copper oxide nanoparticles in soybean (*Glycine max* L.) root development and lignification of root cells. Biol Trace Elem Res 162(13):342–352
- <span id="page-13-13"></span>Nair PMG, Chung IM (2014b) Impact of copper oxide nanoparticles exposure on *Arabidopsis thaliana* growth, root system development, root lignification, and molecular level changes. Environ Sci Pollut Res 21:12709–12722
- <span id="page-13-14"></span>Nair PMG, Chung IM (2015) Study on the correlation between copper oxide nanoparticles induced growth suppression and enhanced lignification in Indian mustard (*Brassica juncea* L.) Ecotoxicol Environ Safe 113:302–313
- <span id="page-13-7"></span>Nekrasova GF, Ushakova OS, Ermakov AE, Uimin MA, Byzov IV (2011) Effects of copper (II) ions and copper oxide nanoparticles on *Elodea densa* Planch. Russ J Ecol 42:458–463
- <span id="page-13-21"></span>Nelson BC, Johnson ME, Walker ML, Riley KR, Sims CM (2016) Antioxidant cerium oxide nanoparticles in biology and medicine. Antioxidants (Basel) 5(2). doi[:10.3390/antiox5020015](http://dx.doi.org/10.3390/antiox5020015)
- <span id="page-13-16"></span>Ornatska M, Sharpe E, Andreescu D, Andreescu S (2011) Paper bioassay based on ceria nanoparticles as colorimetric probes. Anal Chem 83:4273–4280
- <span id="page-13-0"></span>Ozimek L, Pospiech E, Narine S (2010) Nanotechnologies in food and meat processing. Acta Sci Pol Technol Aliment 9(4):401–412
- <span id="page-13-15"></span>Patil S, Kuiry SC, Seal S, Vanfleet R (2002) Synthesis of nanocrystalline ceria particles for high temperature oxidation resistant coating. J Nanopart Res 4:433–438
- <span id="page-13-3"></span>Prasad R (2014) Synthesis of silver nanoparticles in photosynthetic plants. J Nanopart:Article ID 963961. <http://dx.doi.org/10.1155/2014/963961>
- <span id="page-13-1"></span>Prasad R, Kumar V, Prasad KS (2014) Nanotechnology in sustainable agriculture: present concerns and future aspects. Afr J Biotechnol 13(6):705–713
- <span id="page-13-2"></span>Prasad R, Pandey R, Barman I (2016) Engineering tailored nanoparticles with microbes: quo vadis. WIREs Nanomed Nanobiotechnol 8:316–330. doi[:10.1002/wnan.1363](http://dx.doi.org/10.1002/wnan.1363)
- <span id="page-14-1"></span>Prasad R, Pandey R, Varma A, Barman I (2017) Polymer based nanoparticles for drug delivery systems and cancer therapeutics. In: Kharkwal H, Janaswamy S (eds) Natural polymers for drug delivery. CAB International, Oxfordshire, pp 53–70
- <span id="page-14-16"></span>Priyanka N, Venkatachalam P (2016) Biofabricated zinc oxide nanoparticles coated with phycomolecules as novel micronutrient catalysts for stimulating plant growth of cotton. Adv Nat Sci Nanosci Nanotechnol 7:045018. <http://iopscience.iop.org/2043-6262/7/4/045018>
- <span id="page-14-9"></span>Raho N, Ramirez L, Lanteri ML, Gonorazky G, Lamattina L, ten Have A, Laxalt AM (2011) Phosphatidic acid production in chitosan-elicited tomato cells, via both phospholipase D and phospholipase C/diacylglycerol kinase, requires nitric oxide. J Plant Physiol 168:534–539
- <span id="page-14-4"></span>Rangaraj SR, Gopalu K, Muthusamy P, Rathinam Y, Venkatachalam R, Narayanasamy K (2014) Augmented biocontrol action of silica nanoparticles and *Pseudomonas fluorescens* bioformulant in maize (*Zea mays* L.) RSC Adv 4:8461–8465
- <span id="page-14-15"></span>Rico CM, Morales MI, Barrios AC, McCreary R, Hong J, Lee WY, Nunez J, Peralta-Videa JR, Gardea-Torresdey JL (2013a) Effect of cerium oxide nanoparticles on the quality of rice (*Oryza sativa* L.) grains. J Agric Food Chem 61(47):11278–11285
- <span id="page-14-13"></span>Rico CM, Hong J, Morales MI, Zhao LJ, Barrios AC, Zhang JY, PeraltaVidea JR, Gardea-Torresdey JL (2013b) Effect of cerium oxide nanoparticles on rice: a study involving the antioxidant defense system and in vivo fluorescence imaging. Environ Sci Technol 47(11):5635–5642
- <span id="page-14-14"></span>Rico CM, Morales MI, McCreary R, Castillo-Michel H, Barrios AC, Hong J, Alejandro T, Lee WY, Armando VR, Peralta-Videa JR, Gardea-Torresdey JL (2013c) Cerium oxide nanoparticles modify the antioxidative stress enzyme activities and macromolecule composition in rice seedlings. Environ Sci Technol 47:14110–14118
- <span id="page-14-3"></span>Rico CM, Peralta-Videa JR, Gardea-Torresdey JL (2015) Chemistry, biochemistry of nanoparticles, and their role in antioxidant defense system in plants. In: Nanotechnology and plant sciences. Springer, Cham, pp 1–17
- <span id="page-14-17"></span>Robert-Seilaniantz A, Grant M, Jones JD (2011) Hormone crosstalk in plant disease and defense: more than just jasmonate–salicylate antagonism. Annu Rev Phytopathol 49:317–343
- <span id="page-14-0"></span>Saboktakin MR (2012) Chapter 3 Starch nanocomposite and nanoparticles: biomedical applications. In: Modern trends in chemistry and chemical engineering. Apple Academic Press, Oakville, pp 48–73
- <span id="page-14-8"></span>Saharan V, Mehrotra A, Khatik R, Rawal P, Sharma SS, Pal A (2013) Synthesis of chitosan based nanoparticles and their in vitro evaluation against phytopathogenic fungi. Int J Biol Macromol 62:677–683
- <span id="page-14-7"></span>Saharan V, Sharma G, Yadav M, Choudhary MK, Sharma SS, Pal A, Raliya R, Biswas P (2015) Synthesis and in vitro antifungal efficacy of Cu-chitosan nanoparticles against pathogenic fungi of tomato. Int J Biol Macromol 75:346–353
- <span id="page-14-10"></span>Servin AD, Morales MI, Castillo-Michel H, Hernandez-Viezcas JA, Munoz B, Zhao LJ, Nunez JE, Peralta-Videa JR, Gardea-Torresdey JL (2013) Synchrotron verification of  $TiO<sub>2</sub>$  accumulation in cucumber fruit: a possible pathway of  $TiO<sub>2</sub>$  nanoparticle transfer from soil into the food chain. Environ Sci Technol 47:11592–11598
- <span id="page-14-11"></span>Shaw AK, Hossain Z (2013) Impact of nano-CuO stress on rice (*Oryza sativa* L.) seedlings. Chemosphere 93:906–915
- <span id="page-14-12"></span>Shaw AK, Ghosh S, Kalaji HM, Bosa K, Brestic M, Zivcak M, Hossain Z (2014) Nano-CuO stress induced modulation of antioxidative defense and photosynthetic performance of syrian barley (*Hordeum vulgare* L.) Environ Exp Bot 102:37–47
- <span id="page-14-6"></span>Shweta, Tripathi DK, Singh S, Singh S, Dubey NK, Chauhan DK (2016) Impact of nanoparticles on photosynthesis: challenges and opportunities. Mater Focus 5(5):405–411
- <span id="page-14-5"></span>Singh VP, Singh S, Kumar J, Prasad SM (2015) Investigating the roles of ascorbate-glutathione cycle and thiol metabolism in arsenate tolerance in ridged Luffa seedlings. Protoplasma 252:1217–1229
- <span id="page-14-2"></span>Singh S, Vishwakarma K, Singh S, Sharma S, Dubey NK, Singh VK, Liu S, Tripathi DK, Chauhan DK (2017a) Understanding the plant and nanoparticle interface at transcriptomic and proteomic level: a concentric overview. Plant Gene. <http://dx.doi.org/10.1016/j.plgene.2017.03.006>
- <span id="page-15-1"></span>Singh S, Tripathi DK, Singh S, Sharma S, Dubey NK, Chauhan DK, Vaculík M (2017b) Toxicity of aluminium on various levels of plant cells and organism: a review. Environ Exp Bot 137:177–193
- <span id="page-15-4"></span>Smirnova EA, Gusev AA, Zaitseva ON, Lazareva EM, Onishchenko GE, Kuznetsova EV, Tkachev AG, Feofanov AV, Kirpichnikov MP (2011) Multi-walled carbon nanotubes penetrate into plant cells and affect the growth of *Onobrychis arenaria* seedlings. Acta Nat 3(1):99–106
- <span id="page-15-15"></span>Stambouli AB, Traversa E (2002) Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. Renew Sust Energy Rev 6:433–455
- <span id="page-15-0"></span>Suganeswari M, Shering MA, Bharathi P, JayaSutha J (2011) Nanoparticles: a novel system in current century. Int J Pharm Biol Sci Arch 2(2):847–854
- <span id="page-15-12"></span>Suriyaprabha R, Karunakaran G, Kavitha K, Yuvakkumar R, Rajendran V, Kannan N (2014) Application of silica nanoparticles in maize to enhance fungal resistance. IET Nanobiotechnol 8(3):133–137
- <span id="page-15-16"></span>Tan F, Zhang YJ, Wang JL, Wei JY, Cai Y, Qian XH (2008) An efficient method for dephosphorylation of phosphopeptides by cerium oxide. J Mass Spectrom 43:628–632
- <span id="page-15-3"></span>Tan XM, Lin C, Fugetsu B (2009) Studies on toxicity of multi-walled carbon nanotubes on suspension rice cells. Carbon 47:3479–3487
- <span id="page-15-17"></span>Thwala M, Musee N, Sikhwivhilu L, Wepener V (2013) The oxidative toxicity of Ag and ZnO nanoparticles towards the aquatic plant *Spirodela punctuta* and the role of testing media parameters. Environ Sci Process Impacts 15:1830–1843
- <span id="page-15-5"></span>Tripathi DK, Singh VP, Kumar D, Chauhan DK (2012a) Impact of exogenous silicon addition on chromium uptake, growth, mineral elements, oxidative stress, antioxidant capacity, and leaf and root structures in rice seedlings exposed to hexavalent chromium. Acta Physiol Plant 34(1):279–289
- <span id="page-15-6"></span>Tripathi DK, Singh VP, Kumar D, Chauhan DK (2012b) Rice seedlings under cadmium stress: effect of silicon on growth, cadmium uptake, oxidative stress, antioxidant capacity and root and leaf structures. Chem Ecol 28(3):281–291
- <span id="page-15-7"></span>Tripathi DK, Chauhan DK, Kumar D, Tiwari SP (2012c) Morphology, diversity and frequency based exploration of phytoliths in *Pennisetum typhoides*Rich. Natl Acad Sci Lett 35(4):285–289
- <span id="page-15-8"></span>Tripathi DK, Kumar R, Pathak AK, Chauhan DK, Rai AK (2012d) Laser-induced breakdown spectroscopy and phytolith analysis: an approach to study the deposition and distribution pattern of silicon in different parts of wheat (*Triticum aestivum* L.) plant. Agric Res 1(4):352–361
- <span id="page-15-9"></span>Tripathi DK, Mishra S, Chauhan DK, Tiwari SP, Kumar C (2013) Typological and frequency based study of opaline silica (phytolith) deposition in two common Indian *Sorghum* L. species. Proc Natl Acad Sci India Sect B Biol Sci 83(1):97–104
- <span id="page-15-10"></span>Tripathi DK, Prasad R, Chauhan DK (2014a) An overview of biogenic silica production pattern in the leaves of *Hordeum vulgare* L. Indian J Plant Sci 3(2):167–177
- Tripathi DK, Singh VP, Gangwar S, Prasad SM, Maurya JN, Chauhan DK (2014b) Role of silicon in enrichment of plant nutrients and protection from biotic and abiotic stresses. In: Improvement of crops in the Era of climatic changes. Springer, New York, pp 39–56
- <span id="page-15-13"></span>Tripathi DK, Singh VP, Prasad SM, Chauhan DK, Dubey NK (2015a) Silicon nanoparticles (SiNp) alleviate chromium (VI) phytotoxicity in *Pisum sativum* (L.) seedlings. Plant Physiol Biochem 96:189–198
- <span id="page-15-11"></span>Tripathi DK, Singh VP, Prasad SM, Chauhan DK, Dubey NK, Rai AK (2015b) Silicon-mediated alleviation of Cr (VI) toxicity in wheat seedlings as evidenced by chlorophyll florescence, laser induced breakdown spectroscopy and anatomical changes. Ecotoxicol Environ Saf 113:133–144
- <span id="page-15-2"></span>Tripathi DK, Gaur S, Singh S, Singh S, Pandey R, Singh VP, Sharma NC, Prasad SM, Dubey NK, Chauhan DK (2016a) An overview on manufactured nanoparticles in plants: uptake, translocation, accumulation and phytotoxicity. Plant Physiol Biochem. [http://dx.doi.org/10.1016/j.](http://dx.doi.org/10.1016/j.plaphy.2016.07.030) [plaphy.2016.07.030](http://dx.doi.org/10.1016/j.plaphy.2016.07.030)
- <span id="page-15-14"></span>Tripathi DK, Singh S, Singh VP, Prasad SM, Chauhan DK, Dubey NK (2016b) Silicon nanoparticles more efficiently alleviate arsenate toxicity than silicon in maize cultiver and hybrid differing in arsenate tolerance. Front Environ Sci 4:46
- <span id="page-16-5"></span>Tripathi DK, Singh VP, Ahmad P, Chauhan DK, Prasad SM (eds) (2016c) Silicon in plants: advances and future prospects. CRC Press, Boca Raton
- <span id="page-16-6"></span>Tripathi DK, Singh S, Singh S, Chauhan DK, Dubey NK, Prasad R (2016d) Silicon as a beneficial element to combat the adverse effect of drought in agricultural crops. In: Water stress and crop plants: a sustainable approach. Wiley Blackwell, Chichester/Oxford, pp 682–694
- <span id="page-16-9"></span>Tripathi DK, Singh VP, Prasad SM, Dubey NK, Chauhan DK, Rai AK (2016e) LIB spectroscopic and biochemical analysis to characterize lead toxicity alleviative nature of silicon in wheat (*Triticum aestivum* L.) seedlings. J Photochem Photobiol B Biol 154:89–98
- <span id="page-16-0"></span>Tripathi DK, Singh S, Singh S, Srivastava PK, Singh VP, Singh S, Prasad SM, Singh PK, Dubey NK, Pandey AC, Chauhan DK (2017a) Nitric oxide alleviates silver nanoparticles (AgNps) induced phytotoxicity in *Pisum sativum* seedlings. Plant Physiol Biochem 110:167–177
- <span id="page-16-1"></span>Tripathi DK, Tripathi A, Shweta SS, Singh Y, Vishwakarma K, Yadav G, Sharma S, Singh VK, Mishra RK, Upadhyay RG, Dubey NK (2017b) Uptake, accumulation and toxicity of silver nanoparticle in autotrophic plants, and heterotrophic microbes: a concentric review. Front Microbiol 8
- <span id="page-16-2"></span>Tripathi DK, Mishra RK, Singh S, Singh S, Vishwakarma K, Sharma S, Singh VP, Singh PK, Prasad SM, Dubey NK, Pandey AC (2017c) Nitric oxide ameliorates zinc oxide nanoparticles phytotoxicity in wheat seedlings: implication of the ascorbate–glutathione cycle. Front Plant Sci 8
- <span id="page-16-7"></span>Tripathi DK, Shweta SS, Yadav V, Arif N, Singh S, Dubey NK, Chauhan DK (2017d) Silicon: a potential element to combat adverse impact of UV-B in plants. In: UV-B radiation: from environmental stressor to regulator of plant growth, vol 175. Wiley Blackwell, Oxford/Chichester/ Hoboken
- <span id="page-16-8"></span>Tripathi DK, Singh S, Singh VP, Prasad SM, Dubey NK, Chauhan DK (2017e) Silicon nanoparticles more effectively alleviated UV-B stress than silicon in wheat (*Triticum aestivum*) seedlings. Plant Physiol Biochem 110:70–81
- <span id="page-16-12"></span>Trovarelli A (1996) Catalytic properties of ceria and CeO<sub>2</sub> containing materials. Catal Rev 38:439–520
- <span id="page-16-15"></span>Wang H, Wu F, Meng W, White JC, Holden PA, Xing B (2013) Engineered nanoparticles may induce genotoxicity. Environ Sci Technol 47:13212–13214
- <span id="page-16-11"></span>Wang SL, Liu HZ, Zhang YX, Xin H (2015) The effect of CuO NPs on reactive oxygen species and cell cycle gene expression in roots of rice. Environ Toxicol Chem 34:554–561
- <span id="page-16-4"></span>Xing K, Zhu X, Peng X, Qin S (2015) Chitosan antimicrobial and eliciting properties for pest control in agriculture: a review. Agron Sustain Dev. Springer Verlag/EDP Sciences/INRA 35(2):569–588
- <span id="page-16-13"></span>Xu C, Lin Y, Wang J, Wu L, Wei W, Ren J, Qu X (2013) Nanoceria triggered synergetic drug release based on CeO<sub>2</sub>capped mesoporous silica host-guest interactions and switchable enzymatic activity and cellular effects of  $CeO<sub>2</sub>$ . Adv Healthc Mater 2:1591–1599
- <span id="page-16-10"></span>Yadav L, Tripathi RM, Prasad R, Pudake RN, Mittal J (2017) Antibacterial activity of Cu nanoparticles against *E. coli, Staphylococcus aureus* and *Pseudomonas aeruginosa*. Nano Biomed Eng 9(1):9–14. doi:[10.5101/nbe.v9i1.p9-](http://dx.doi.org/10.5101/nbe.v9i1.p9-)
- <span id="page-16-14"></span>Zhao LJ, Peng B, Hernandez-Viezcas JA, Rico C, Sun YP, Peralta-Videa JR, Tang XL, Niu GH, Jin LX, Varela-Ramirez A, Zhang JY, GardeaTorresdey JL (2012) Stress response and tolerance of *Zea mays* to  $CeO<sub>2</sub>$  nanoparticles: cross talk among  $H<sub>2</sub>O<sub>2</sub>$ , heat shock protein, and lipid peroxidation. ACS Nano 6(11):9615–9622
- <span id="page-16-3"></span>Zhao LJ, Hernandez-Viezcas JA, Peralta-Videa JR, Bandyopadhyay S, Peng B, Munoz B, Keller AA, Gardea-Torresdey JL (2013) ZnO nanoparticle fate in soil and zinc bioaccumulation in corn plants (*Zea mays*) influenced by alginate. Environ Sci Process Impacts 15:260–266