

# Nanotechnology in agriculture, livestock, and aquaculture in China. A review

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**Abstract** Nanoscience emerged in the late 1980s and is developed and applied in China since the middle of the 1990s. Although nanotechnologies have been less developed in agronomy than other disciplines, due to less investment, nanotechnologies have the potential to improve agricultural production. Here, we review more than 200 reports involving nanoscience in agriculture, livestock, and aquaculture. The major points are as follows: (1) nanotechnologies used for seeds and water improved plant germination, growth, yield, and quality. (2) Nanotechnologies could increase the storage period for vegetables and fruits. (3) For livestock and poultry breeding, nanotechnologies improved animals immunity, oxidation resistance, and production and decreased antibiotic use and manure odor. For instance, the average daily gain of pig increased by 9.9–15.3 %, the ratio of feedstuff to weight decreased by 7.5–10.3 %, and the diarrhea rate decreased by 55.6–66.7 %. (4) Nanotechnologies for water disinfection in fishpond increased water quality and increased yields and survivals of fish and prawn. (5) Nanotechnologies for pesticides increased pesticide performance threefold and reduced cost by 50 %. (6) Nano urea increased the agronomic efficiency of nitrogen fertilization by 44.5 % and the grain yield by 10.2 %, versus normal urea. (7) Nanotechnologies are widely used for rapid detection and diagnosis, notably for clinical examination, food safety testing, and animal epidemic

surveillance. (8) Nanotechnologies may also have adverse effects that are so far not well known.

**Keywords** Nanoscience and nanotechnology · Application · Agriculture · Livestock · Aquaculture · Potential risks

## Contents

- 1 Introduction
  - 1.1 Concept and definition of nanotechnologies
  - 1.2 Function of nanotechnologies
  - 1.3 Mechanisms of nanotechnologies
  - 1.4 Photocatalyst sterilization and promotion of photosynthesis
  - 1.5 The conditions of nanotechnologies in China
- 2 Application of nanotechnologies in agricultural production
  - 2.1 Nanotechnologies used for vegetables
  - 2.2 Application of nanotechnologies in fruits
  - 2.3 Application of nanotechnologies in rice and other food crops
- 3 Application of nanotechnologies in livestock and poultry breeding
  - 3.1 Application of nanotechnologies in chicken breeding
  - 3.2 Application of nanotechnologies in pig industry
- 4 Application of nanotechnologies in aquaculture
  - 4.1 Nanotechnologies and fishery industry
  - 4.2 Nanotechnologies in controlling of aquatic diseases
- 5 Development of new type of nanotechnologies pesticides and plant protection
  - 5.1 Development of new type of nano pesticides
  - 5.2 Pesticides dilution with nanotechnologies treated water
  - 5.3 Nanotechnologies in inhibition of pathogens
  - 5.4 Nanotechnologies application in plant protection

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- 5.5 Nanotechnologies on microorganisms and insects
- 6 Nano fertilizers and effects on crops
  - 6.1 Effects of nano fertilizer on rice crop
  - 6.2 Effects of nano fertilizer on other crops
- 7 Nanotechnologies in detection of hazardous substance and environment protection
  - 7.1 Detection of diseases
  - 7.2 Detection of mycotoxins
  - 7.3 Detection of pesticide residues and degradation
  - 7.4 Nanotechnologies used in environmental protection
- 8 Potential risks of nanotechnologies
  - 8.1 Effects of nanotechnologies on human health
  - 8.2 Nanotechnologies and environmental issues
  - 8.3 Social risks of nanotechnologies
- 9 Conclusion
- Acknowledgements
- References

## 1 Introduction

### 1.1 Concept and definition of nanotechnologies

The term “nanomaterial” is based on the prefix “nano,” which originates from the Greek word meaning “dwarf.” More precisely, the word nano means  $10^{-9}$  or one billionth of a meter. The word nanomaterial is generally used for materials with a size ranging between 1 and 100 nm (Rai and Ingle 2012). Nanotechnology may be used for observing, measuring, manipulating, and manufacturing objects at the nanometer (nm) scale. A nanometer is an SI (standing for *Système International d’Unités* in French) unit of length referring to  $10^{-9}$  or a distance of one billionth of a meter (Mongillo 2007; Can et al. 2011). These new materials are manufactured to have unique physical or chemical properties, which arise from their small size, shape, surface area, conductivity, or surface chemistry, and have been applied in numerous ways in fields such as textiles, electronics, engineering, and medicine (Smith et al. 2007). Nanotechnologies involve the understanding and control of matter at the nanoscale, namely, at dimensions between approximately 1–100 nm, where unique phenomena such as improved physical, chemical, and biological properties may enable novel applications (Vyom et al. 2012). Since 2000, the governments of various countries, institutional frameworks, and enterprises all have attached great importance to the research, development, and application of nanotechnologies. Some countries have also enacted relevant strategies or plans and invested substantial sums of funds to seize the strategic highland of nanotechnologies.

### 1.2 Function of nanotechnologies

Nanotechnologies, information science technology, and life science and technology are the current mainstays of science development; the development of which will enable human society, our living environment, and science and technology themselves to attain a higher state of development. It has also been predicted that in the next 20 to 30 years, nanotechnologies will fundamentally change the understanding and conditions of mankind and create new development opportunities for physics, chemistry, materials, biology, medical science, and other fields. Nanotechnologies can be used to operate genes freely, to produce plant and animal species with its excellent properties, and nanoparticles can be used as vectors for treating various diseases. When nano biology develops to a certain level, nanotechnologies can be used to produce nano biological cells with recognition ability and can absorb biological medicine which can inhibit cancer cells, which may then be injected into the human body to directly destroy cancer cells.

Nanotechnologies hold great potential for creating new materials with enhanced properties. A number of nanotech-based products are finding applications in industries such as medical devices, imaging, sports, biosensing, electronics, drugs, environmental cleanup, cosmetics and sunscreens (NCPI 2011; USEPA 2007), agriculture, textiles, food, etc. (Sharon et al. 2010; Sastry et al. 2011). In the future, the global economy will be increasingly influenced by nanotechnologies, as more products containing nanotechnologies move from research and development into production and commerce.

Conventional techniques of nanoparticle synthesis, which usually employ atomic, molecular, and particulate processing in vacuum or in a liquid medium, are capital intensive (Mandal et al. 2006; Anandan et al. 2008) and inefficient in terms of material and energy usage (Pugazhenthiran et al. 2009). A large number of nanoparticles were synthesized by using fungi and widely used in all professions and trades at home and abroad (Kashyap et al. 2013).

### 1.3 Mechanisms of nanotechnologies

The changes of water clusters treated with nanotechnologies through ultraviolet absorption spectrum and nuclear magnetic resonance (NMR) spectroscopy. The light absorption of water treated with nanotechnologies on ultraviolet absorption spectrum was strengthened at the wave band of 190–325 nm, which illustrated that the structure and energy state of water molecule had changed.  $^{17}\text{O}$ -NMR half peak width of water became narrow and the chemical shift decreased and moved toward low field. Water treated with nanotechnologies had smaller micelle and higher activity (Liu et al. 2008a).

The half peak width size of water  $^{17}\text{O}_2$ -NMR reflects the degree of association of water, which is the size of molecules (Li et al. 2002). When the half peak width is large, the molecule size is also large and vice versa (Li et al. 2004). The half peak width size of water without nanotechnologies treatment is 126 Hz; however, the half peak width sizes of water with treatments of different nano devices are 68–124 Hz, which is smaller than those of untreated water half peak width (decreased by 1.59–46.03 %), showing that the molecule size of water becomes smaller after nanotechnology treatment. The absorption spectrum and nuclear magnetic resonance results demonstrated that the associative structure of the molecules was changed in water after nanotechnology (devices) treatment. The half peak width of the  $^{17}\text{O}_2$ -NMR became narrow, chemical displacement was decreased and moved to lower fields, and activity of water was enhanced (Liu et al. 2008a).

#### 1.4 Photocatalyst sterilization and promotion of photosynthesis

Titanium dioxide ( $\text{TiO}_2$ ) is a kind of photocatalyst, it can stimulate electrons on material surfaces under ultraviolet radiation, which in turn may continuously induce energy transition, then causing electrons to escape and form a hole (positive hole), with strong oxidation ability and electrons with strong reducing ability.

The photochemical reaction equation of hole/electron pair produced by photocatalyst ( $\text{TiO}_2$ ) under light is as follows:  $\text{TiO}_2 + \text{light energy (hv)} \rightarrow \text{electron (e}^-) + \text{positive hole (h}^+)$ . The hole/electron reacts with the object surface and water in the air, and then reactive free radicals (positive hole) are produced as follows:  $(\text{h}^+) + \text{water molecules (H}_2\text{O)} \rightarrow \text{OH} + \text{H}^+$ ,  $\text{electron (e}^-) + \text{oxygen (O}_2) \rightarrow \text{reactive oxygen species (O}_2^-)$ . The oxidation-reduction reaction takes place between the hole/electron pairs produced by photocatalyst reaction and organics on the matter surface and in the air, which may then be completely oxidized to water and other innocuous substances. On the other hand, reactive oxygen nanotechnologies, hydroxyl radicals [HO], and other active substances can be generated after the reaction of hole/electron pairs and on the matter surface and water in the air (Zhao et al. 2005). The active substances have a strong oxygenation effect, which not only can oxidize and destroy the cell membranes of the organics of bacteria and fungi, solidify viral proteins, and kill bacteria, but also can decompose harmful complexes released by the microorganisms which have been killed. Furthermore, the active substances can completely oxidize and destroy organic chemical pollutants, so as to achieve effects of environmental cleansing and deodorization. The antibacterial property test results of the photocatalyst-spraying agents also indicated that the respective average bacteriostasis rates on *Staphylococcus aureus*, *Escherichia coli*, and *Candida*

*albicans* at 24 h were 97.7, 97.3, and 93.3 % after treatment with photocatalyst-spraying agents.

Photosynthesis refers to a process in which green plants use solar energy and convert carbon dioxide and water into carbohydrates and release oxygen.  $2\text{H}_2\text{O} + \text{chloroplast} + \text{light energy} \rightarrow 4\text{H} + \text{O}_2 + 4\text{e}^- - \text{CO}_2 + \text{H}_2\text{O} + \text{green cells} + \text{light energy} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2$ . Under ultraviolet light,  $\text{TiO}_2$  can independently hydrolyze light into electrons, protons, and oxygen, in which the produced electron and proton go into an electron transfer chain of plants in the light reaction stage, thus improving the speed of photosynthesis (Zhao et al. 2005; Zhang et al. 2008c). Due to the fact that the photocatalyst  $\text{TiO}_2$  is not involved in the above reaction process, the reaction may be repeated and the photocatalyst may play a role for a long period of time. Compared with that of the general antibacterial agent silver and copper, the  $\text{TiO}_2$  has much more thorough bactericidal efficacy, and the sterilization effect may reach as high as 99.997 %.

#### 1.5 The conditions of nanotechnologies in China

The research on nanotechnologies date from the late 1980s, and development and application began in the middle of 1990s in China. At present, significant progress in the aspects of leading edge fundamental research of nanoscience, application and achievement transformation, and infrastructure construction have been obtained. China already has become world nanometer scientific and technological power; partial fundamental researches have occupied the international advanced level. A number of published papers which recorded by science citation index (SCI) which concern nanotechnologies published by Chinese scientists have exceeded the American's, ranked no. 1, and the papers cited frequency ranked no. 2 in the world. The number of application for or authorization of patent for invention related to the nanoscience was increased significantly, ranked no. 2 in the world (Nanometer science and technology in China 2013).

The number of patent for invention related to the fields of superfine materials and nanotechnology which have opened to the public reached 1024: among them 827 were referring to the materials, which accounted for 80.8 % and occupied absolute dominant position; 28 (2.7 %) were referring to electron; 41 (4.0 %) were referring to medicine and drug; and 128 (12.5 %) were referring to others. The above results demonstrated that the investment in the research of nanomaterials is larger, while the research on the nano electronics, nano medicine, and nano pharmaceuticals were weak. The investment of nanotechnologies in agricultural fields is much less, and the nano technologies and nano products were available for using less as well. However, there are some nanotechnologies and nano products which were used in agriculture, animal husbandry, and aquaculture industry, and remarkable effects were achieved.

Nanotechnologies or the water treated with nanotechnologies used for seeds soaking, irrigation, agrochemicals dilution, and treating fertilizer, the seed germination rate and germination state were increased; seedling quality improved; and crop yields increased and improved the quality of agro-products. The pesticide performances and their control efficacies would be enhanced when the nanotechnologies were used for preparation of agrochemical suspension. The dosage will be reduced (Ji et al. 2002).

When nanotechnologies were used for animal husbandry, the appetites of livestock and poultry were improved, daily gain increased, the feed to gain ratio decreased, the diarrhea ratio and death rate of weanling piglets reduced. The contaminants in the livestock farm will be reduced and the odor alleviated and the sanitation vastly improved. Due to the nanometer biosensors possess the advantage of high sensitivity, accuracy, quick, and reliability, it can be used for the supervision and detection of noxious substances in the environment, agro-products, food and feed, etc., such as pesticides and heavy metal and so on. The problem of pesticide residue will be resolved by using nanotechnologies finally.

Nanotechnologies have fortissimo ability for inhibition or killing various kinds of microbes; it can be used for disinfection of the environment and a variety of appliances. The control efficiency of nanoscale pesticides (biopesticides) is one to threefold higher than that of ordinary pesticide when the dosage was the same while the cost reduced a half.

Although, nanotechnologies possess tremendous advantages and wide application prospect, and it has already brought or will bring great economic, social, and ecological benefits. However, if things are always divided into two, it cannot be denied that nanotechnologies show enormous potential risk as well. The nanotechnologies have potential hazard to human and animals and affect their health and security; it constitutes a danger to the environmental safety. In social risks, the nanotechnologies mainly show toxicity to the cells, microbes, animals, lower plants and higher plants, etc. Some harm of nanotechnologies have been confirmed, and some are not clear and need to be further studied and testified.

In China, nanotechnologies have been applied in the fields of industry, agriculture, medicine, and environmental protection. The nano devices presently used in China mainly include the following: Qiangdi nanometer 863 biont growth-promoting device (hereinafter referred to “nano-863”); nano ceramic pot; nano net; nano film; nano selenium; nano TiO<sub>2</sub>; nano pottery disc; nano biotechnology slow/controlled release fertilizer (or “nano synergism fertilizer”); tombarthite nano thin film light spraying fertilizer; nano selenium-nano zinc added to animal feed; nano zinc oxide (ZnO) fungicides; photocatalyst (TiO<sub>2</sub>) disinfectant; copper (ferric) salt solution and nano montmorillonite disinfectants produced through absorption and ion exchange reaction used for livestock and poultry places (homes) and utensil disinfection; nano silver

and nano CuO for antibacterial and killing of bacteria; fungicidal, bactericidal, and anti-corrosion nano SiO<sub>2</sub>; quasi-nanoscale silver; new type nano silicon nanoscale oxide (SiO<sub>x</sub>) for environmental and health disinfection and plant protection; nano calcium carbonate, copper-bearing montmorillonite (Cu<sup>2+</sup>-MMT) used for aquaculture; composite nano capsule tablet with the main components of TiO<sub>2</sub>, ZnO and Fe<sub>3</sub>O<sub>4</sub>@ZrO<sub>2</sub> used for enrichment and adsorption of organic phosphorus (OP) pesticides to attain the degradation of pesticides; and hydrolyzed collagen, alginate, and nano TiO<sub>2</sub>-nano SiO<sub>2</sub> composite materials, used in preservation film for fruits.

Nano-863 is an agricultural high-tech product and most widely used in China at present. The nanotechnologies product nano-863 is produced by adding nanomaterials with strong light-absorbing properties and high temperature sintering with a ceramic material as a carrier. It has been widely used in the fields of crop cultivation and breeding of livestock and aquaculture (Fig. 1).

## 2 Application of nanotechnologies in agricultural production

The functions of nanotechnologies in the promotion biological metabolism have been applied in many aspects. For example, seed treating or irrigation (watering) with treated water by nanotechnology devices can promote the crop growth, increase the yield, and improve the quality of many crop products, including cereal crops and cash crops. Although nanotechnology application in food and agriculture is in its budding stage, we hope to see increasing uses of tools and techniques developed by nanotechnologies in agricultural fields in the next few years (Tuteja and Singh Gill 2013).



**Fig. 1** Different types of biological assistant growth apparatus ceramic discs. Qiangdi nano-863 (the biggest green one in the center), Suzhou Zhongchi (a, b, c, and d discs around)

## 2.1 Nanotechnologies used for vegetables

The seeds of legumes (cowpea), cabbage (brassica) and cucumber were soaked with the water which was treated by nano-863. The seeds were treated for 2 h for legumes, 4 h for brassica, and 12 h for cucumber. The average of germination rate, germination state, bud length, bud diameter, and bud fresh weight of various vegetable seeds after soaking with nano-treated water were all higher than those of the seeds soaked with pure water (control), but the increased degrees of the different crop seeds varied greatly (Fang et al. 2004) (Table 1). The average percentage of germination of treated cowpea seeds was 25.8 % higher than that of the control group, and the germination state was improved to 30.7 %. The water treated with nano-863 was used for watering and fertilizing, the germinating state was one to two times higher, the total number of main leaves was 90 % more than that of the control group, and the disease resistance ability of flowers was enhanced. When the garlic were soaked in nano-863-treated water, after 20 days of treatment, the heights of the garlic bolts were 5 cm longer than those of the control group.

The effects of nanotechnologies of TiO<sub>2</sub>-ZnO compound on nitrate, nitrite, and vitamin C content were studied in vegetable. The nanotechnology device can reduce the nitrate and nitrite content of cabbage. And, the decrease was positively correlated to the treatment time. The nanotechnology device has no effect on the vitamin C content in vegetables (Zhang et al. 2008a).

## 2.2 Application of nanotechnologies in fruits

The superiority of nanotechnologies has been gradually acknowledged in the research fields of preservation of fruits and vegetables. Furthermore, the introduction of nanotechnologies into coating preservation of fruits and vegetables for fresh keeping has also been attempted (Ma and Gan 2004). The field of nanotechnologies in preservation of fruits and vegetables is still in its initial stage, so further investigation, discovery, and research breakthrough were required. Nanoparticle has a certain application prospect in the coating preservation of fruits. The effect of keeping nanoparticle complex latex fresh was investigated by coating loquat and cherry with hydrolyzed collagen/sodium alginate. Decay indexes, respiratory intensity, water losses, total acid, and soluble solid were detected during preservation. Experimental results demonstrated that the complex latex can reduce water losses and decay indexes of loquat and control its respiratory intensity. The complex latex using sodium hexametaphosphate to disperse nano-SiO<sub>x</sub> was more effective than others. This was also confirmed in preservation experiment of cherries (Jia et al. 2008).

Nano-preserved fruit wax can improve fruit sensory quality. In the next 5 years, the handling after harvesting and

**Table 1** Effect of soaking seeds with treated water by nano-863 on different vegetable seeds germination rate

Vegetable seed	Treatment	Treatment time	Average rate of germination (%)	Increased germination rate of A than B (%)	Average germination potential (%)	Increased germination potential of A than B (%)	Increased sprout length of A than B (%)	Increased sprout diameter of A than B (%)	Increased fresh weight of A than B (%)
Cowpea	A	2 h	91.39	5.15 <sup>a</sup>	81.70	82.16 <sup>b</sup>	61.3 <sup>b</sup>	8.8 <sup>a</sup>	23.5 <sup>b</sup>
	B		86.91		44.85				
Kidney bean	A		89.10	6.99 <sup>a</sup>	78.40	218.44 <sup>b</sup>	30.5 <sup>b</sup>	6.9 <sup>a</sup>	5.9 <sup>a</sup>
	B		82.87		24.62				
Pakchoi	A	4 h	81.50	12.62 <sup>b</sup>	58.70	42.06 <sup>b</sup>	50.0 <sup>b</sup>	9.8 <sup>a</sup>	2.6
	B		72.37		41.32				
Cucumber	A	12 h	96.00	4.50	71.00	3.41	23.8 <sup>b</sup>	8.2 <sup>a</sup>	3.0
	B		91.87		68.66				
Pumpkin	A		94.00	16.96 <sup>a</sup>	67.00	15.74 <sup>b</sup>	10.1 <sup>b</sup>	7.4 <sup>a</sup>	3.7
	B		80.37		57.89				

The data were statistical analysis of Data Processing System (Tang 2013) and Duncan's multiple comparison

<sup>a</sup> 5 % significantly different

<sup>b</sup> 1 % significantly different

waxing rate of China's fruit will rise from the current 5 to 40 %. The estimation quantity of treatment fruit in 1 year may attain 24 million tons. However, the current annual demand of fruits with nanotechnology film coating in preservation is 48 thousand tons; thus, it has a broad market prospect. A new nano SiO<sub>x</sub> fruit preservation wax, which is based on the film-forming agent with natural animal and plant wax source, has been developed and used in China as fruit wax. Silicon nano-scale oxide (SiO<sub>x</sub>) and methyltrimethoxysilane are used as the O<sub>2</sub>/CO control material, coupling agent, and dispersing agent, and imazalil and plant growth regulator are respectively applied as the anti-mildew and anti-staling agents. The product not only has effects of common fruit wax preservation, fresh keeping, inhibition of water evaporation, and protection from microbial invasion, but also strengthens control of breathing, metabolism regulation, and anti-mold, which can greatly improve the perceptual qualities and market competitiveness of fruits. At present, the new nano SiO<sub>x</sub> fruit wax has been widely applied in the fruit production regions of several provinces in China. Mass production was carried out for only 2 months, and 18 tons of fruit wax has been sold, and 18 thousand tons of fruit has been treated.

The products of nanotechnologies were used as fruit anti-septic. SiO<sub>2</sub> hydrosol can effectively inhibit the infection of cucumber gray mold fungus *Botrytis cinerea*. When the concentration of SiO<sub>2</sub> hydrosol is 1.0 g/L, the control efficiency is 93.5 %, which is close to that of 600 times of Dacotech (95.7 %). When the concentration of SiO<sub>2</sub> hydrosol is 2.0 g/L, the control efficiency is 98.9 %, which is significantly higher than that of Dacotech (Pu et al. 2005). Quasi nano-silver solution can be used as an antimicrobial preservative of tomato juice and tomato-carrot juice mixture (Zhang et al. 2003). Researchers have developed and produced a nano silicon oxide fruit wax for the first time in the world.

### 2.3 Application of nanotechnologies in rice and other food crops

The major research and application of nanotechnologies on crops are rice and wheat. Rice, wheat, and maize are the three major cereal crops in China. Rice (*Oryza sativa*) is one of the most important crops in the world and is the staple food for over half of the world population. The total world production in 2011 was 722.8 million tons (Nair et al. 2013). Both hybrid rice seeds in southern China and conventional japonica rice seeds in northeastern China were soaked with nano-863-treated water. The seed germination and seedling quality were improved, and the yields were significantly increased (Deng 2003; Ma et al. 2007).

Nanotechnologies promoted the growth of rice. Nano-863-treated water was used by different researchers in different areas for soaking rice seeds, treatment of fertilizer, irrigation water, and pesticide preparation, and all of the results

demonstrated that the nano-863-treated water showed enhancing effects on plant growth, development, and yield. Nanotechnologies used in rice production have comprehensive advantages, and in particular, it showed significant enhancing effects on rice growth in the early stages. Nanotechnologies showed enhancing effects on rice seed germination rate and germination states, promoting rice seedling quality and improving its capacity for anti-adversity. The growth process of rice was also in advance, and the yield increasing effect was significant. Therefore, it is an effective measure to cultivate multiple tillers and enhancing seedlings. In paddy field spraying with nano-863-treated water, the rice yield can be increased within a certain range. Compared with that of the control, the rice yield was increased by 342.0–970.5 kg/hm<sup>2</sup> (3.6–12.0 %) (He 2005; Gong and Dong 2012). The rice seed germination state and germination rate were increased significantly when Xinghe nano aerator was used to treat ten different rice varieties (Zhong et al. 2005). After soaking for 3 and 10 days, the germination states were respectively improved by 0.6–4.0 and 0.4–2.7 %. Compared with that of the clean water soaking of seeds, on the fifth day after seed soaking with Xinghe nano aerator, there were no differences in the shoot fresh weight and shoot length and width. However, on the tenth day, the shoot fresh weight, shoot length, and shoot width was increased by different degrees in the seven rice varieties among the ten with nanotechnology treatment. In addition, there were differences in the germination states, germination rate, shoot fresh weight, and shoot length and width of both different varieties and the same variety.

Rice variety of Nipponbare was treated with nano devices for pot experiments. The four nano devices were nano-863, nano ceramic, nano net, and nano film; clean water was used as the control. The results showed that the nano composite functional materials affected the metabolism of rice and promoted seed germination, plant growth, and development, which were most evident in the tillering stage. The biomass of rice in each treatment increased by 30.8–37.4 %, root weight increased by 12.3–35.2 %, and the total root length, surface area, and volume index were greatly increased. The difference of each index became small until the early booting stages, indicating that the enhancing effects of nanotechnologies in early rice seed germination and seedling were better than those of the late growth stage (Wang et al. 2011c); it also demonstrated that nanotechnologies can promote the metabolism of rice seeds and seedlings, early germination and rooting, increase in number of white roots, and increase in root absorption ability. Nanotechnologies also promoted the growth of rice, tillering occurred in advance 3 days than the control, and the number of tillers increased by 4.9–14.0 % (Table 2). The field experiment results demonstrated that rice seeds soaked with nano device could significantly increase rice production by more than 10 %. The tested results showed

**Table 2** Number of rice tiller after treated with different nano biological assistant growth apparatus

Contents	T0/pure water (control)	T1/nano-863	T2/nanoceramic	T3/nanonet	T4/nanopiece
Tillers (no./hill)	10.31	10.88	11.75	11.38	10.81
Tiller increment %	–	5.5	14.0	10.4	4.9

that the head rice ratio and gel consistency were respectively increased by 31.2 and 15.0 % after treatment with nano devices (Liu et al. 2007a; Wang et al. 2011c) (Table 2, Fig. 2).

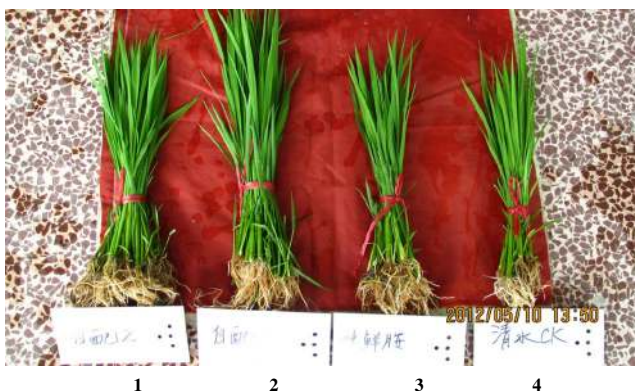
The other experiment results also demonstrated that the growth and development of crops could be promoted by seed soaking and paddy field irrigation with nano device-treated water. The increased extent of rice biomass was 5.6–18.6 %; 0.5–1.4 tillers were increased in each rice plant, with an increase extent of 4.8–14.0 %. Rice root was increased by 5.7–18.8 %. The increased biomass of maize was 12.6–16.5 %, of which chlorophyll content was increased by 6.3–11.0 %. The total absorption nitrogen, phosphorus, and potassium (NPK) of plant was increased, in which phosphorus absorption was particularly evident. The absorbed total phosphorus in rice was increased by 6.2–26.8 %, and that in maize was enhanced by 20.3–23.6 %. However, the nitrogen and potassium percentage contents of plants between each treatment group either did not change significantly or only reduced slightly. Only phosphorus percentage content was increased, the  $P_2O_5$  contents of rice plants in each treatment group were enhanced by 0.3–7.6 %. The  $P_2O_5$  contents of maize plants in each treatment group were enhanced by 6.1–8.7 %. These data suggest that nanotechnologies may increase the chlorophyll content of crops, which is conducive to the promotion of photosynthesis and increasing photosynthate. After treatment of nanotechnologies, the root was more developed and could absorb more nutrients, thereby increasing the biomass. The total absorption content of phosphorus and content of phosphorus in plants were both increased in the nitrogen,

phosphorus, and potassium, which was closely related to the synergistic effect of nano device-treated water on phosphorus (Liu et al. 2007b) (Fig. 3).

From the period of seedling establishment, the various growth stages of rice with nanotechnology treatment were 1–2 days earlier than those of the control group, and the seedling quality was better. Absorption of fertilizer, physiological activity, and function were improved in rice, and the growth vigor and stress resistance abilities were stronger than those of the control. The development process was accelerated, precocity was promoted, and yield was increased. The results of seed inspection and yield measurement demonstrated that the spike number, spike length, grain number per panicle, and 1000-grain weight of per unit area in the treatment areas were all significantly higher than those of the control (Zhang et al. 2007).

Nanotechnologies can influence the gene expression to a certain degree. The  $\gamma$ -ECS gene of which was expressed in leaves and roots, and the transcribing of  $\gamma$ -ECS gene in rice was slightly enhanced by spraying nano silicon on rice seedlings under cadmium (Cd) stress (Wang et al. 2013).

In wheat seeds treated with and without the 399-nm fertilizer, the germination rate were 94 % and 12 %, respectively. The radicle and plumule of the seeds treated without 399-nm fertilizer grew very slowly, while in the seeds treated with 399-nm fertilizer, the wheat seedlings have developed root system and are growing well. The epidermal cells of stem using 399-nm fertilizer are larger and the vascular bundles are



**Fig. 2** Rice seedlings with different treatments. 1. Seeds treated with Suzhou Zhongchi nano device. 2. Seeds treated with Qiangdi nano-863. 3. Seeds treated with prochloraz. 4. Seeds treated with fresh water (control)



**Fig. 3** Jade plant (*Crassula argentea*) treated with nanomaterial and the growth of new leaves were promoted (yellow pot) compared to the control (white pot) (10 days after treatment)

more compact. Besides carbon and oxygen elements, the species and the percentage of elements contained in the wheat seedlings applied with 399-nm fertilizer are more than those without using 399-nm fertilizer (Liu et al. 2009a).

### 3 Application of nanotechnologies in livestock and poultry breeding

Disease is one of the most important risk factors of livestock and poultry breeding. Clean and healthy breeding places are the premise of the healthy growth of livestock and poultry, which is also very important for the safety and health of staff and improvement of the surrounding air and water environments. Selenium (Se) is one of the essential trace elements for animals and has widespread applications in animal production. Moderate Se adding in feed can increase the animal's antioxidant ability and immune function, maintain the health of the animal body, and promote the growth of livestock and poultry. Nano trace element may enter the animal body through direct penetration; therefore, its utilization rate is much higher than that of the ordinary inorganic trace elements. Research has shown that the utilization coefficient of inorganic trace elements was about 30 %, while the utilization coefficient of nano trace element was close to 100 %. If the calcium carbonate was crushed to the nano level, then the absorption and utilization rate of calcium could be significantly improved. It was demonstrated that nano Se has strong effects on improving the health of livestock, poultry, and fish, promoting growth, and improving feed conversion rate and other aspects. Nano Se exhibited strong nutritional and biological effects on improving the growth performance of chicken, pig, and fish and antioxidant abilities. The optimal dosage range of nano Se is also wider than that of selenomethionine and sodium selenite, showing a higher security.

#### 3.1 Application of nanotechnologies in chicken breeding

In recent years, nanotechnologies have been applied more and more in the field of animal breeding. Not only can it improve animal immunity and reduce the use of antibiotics, but also can reduce the manure odor of livestock and poultry, which is conducive to bring environment improvement.

The nano vitamin D3 and ordinary vitamin D3 were added to the feed of laying hens, respectively. On the condition of same feed dosage, the production performance and shinbone quality of hens which are feeding nano vitamin D3 were better than those of feeding ordinary vitamin D3 (Yang et al. 2014). Mannan oligosaccharides nano-liposomes can increase the average daily gain of healthy chickens, lower feed conversion. The average daily weight gain were significantly higher than

flavomycin control group ( $P < 0.01$ ). Thymus index was significantly lower than that of the control group. The nitric oxide levels of chicken plasma in mannan oligosaccharides nano-liposomes were significantly increased ( $P < 0.01$ ) compared with control groups. Mannan oligosaccharides nano-liposomes can regulate the immune function of chicken and play the role of resisting disease and promoting growth (Hu et al. 2012). Nano-selenium has the advantages of high absorption rate, high security, high antioxidant capacity, high egg-laying capacity, and good growth performance, and the range between nutrition dose and toxic dose of nano-selenium is significantly wider than that of sodium selenite. The toxicity of nano-selenium is lower than that of selenomethionine, and its toxicity is currently the lowest of all selenium supplements (Cai et al. 2013).

Nano-863 was used to treat water and feed, which was then given to Israeli recessive white roosters. The results demonstrated that the daily weight increase in the experimental group was 27.9 % higher than that in the control group. The survival rate and economic benefit increased by 2 and 157.8 %, respectively. The ratio of feedstuff to weight increment was decreased by 18.8 %. The chickens in the experimental group were healthy and lively, their appetite was rich, and feathers were lustrous and smooth, while the chickens in the control group had fluffy feathers.

Nano Se has biological characteristics of high oxidation resistance, high immune regulating, high biological activity, and low toxicity. Previous research concerning nano Se in poultry production has mainly concentrated on the oxidation resistance and improvement of production performance of broilers. The addition of Se to the chicken feed is beneficial to the growth and disease resistance of the chickens. When the addition contents of Se in feed were 0.1, 0.2, 0.3, and 0.4 mg/kg, there were no significantly different effects among the three Se sources of sodium selenite ( $\text{Na}_2\text{SeO}_3$ ), selenomethionine, and nano Se on the growth performance of broilers at the same levels ( $P > 0.05$ ). However, when the addition amount of Se was 0.5 mg/kg, the growth performances of the broiler chickens in the nano Se group were significantly higher than those of the selenomethionine and sodium selenite group ( $P < 0.05$ ). Similarly, when the addition contents of Se in feed were 0.1, 0.2, 0.3, and 0.4 mg/kg, there were no significant difference among the effects of the three Se sources on glutathione peroxidase (GPX) activity and total antioxidant capacity (T-AOC) of the sera and tissues of broilers at the same addition level ( $P > 0.05$ ). However, when the addition amount of Se was 0.5 mg/kg, then the effects of selenomethionine and sodium selenite on the activity of glutathione peroxidase and total antioxidant capacity were dramatically reduced in comparison to those with the addition of 0.5 mg/kg of the same source of Se ( $P < 0.05$ ); in addition, the levels of reactive oxygen species and content of malondialdehyde (MDA) were significantly increased



( $P < 0.05$ ), while there were no significant changes in the nano Se group (Cai 2012).

### 3.2 Application of nanotechnologies in pig industry

Diarrhea is a common intestinal disease with high morbidity and mortality, seriously affecting the growth performance and survival of piglets. Due to the restricted use of antibiotics, new feed additives or drugs have been paid more and more attention. Nano-zinc oxide and montmorillonite were widely used as anti-diarrhea agents in piglets (Qing and Xiao 2013). Microelements of Se and Zn are the essential elements for the animals (Zhang 1993; Bian et al. 2010); they are the important additives of feed and prevent diarrhea and death of weanling pigs, and promote healthy growth of fattening pigs. Generally, the Zn element was added in the feed with common high Zn. This leads to the high toxicity to the pig; in addition, the high Zn cannot be absorbed sufficiently and waste the Zn source. Even more serious was that a mass of Zn was discharged with the feces and results in environment pollution. The supplementation of 500 mg/kg of Zn as nano-ZnO was as effective as 2000 mg/kg of Zn from ZnO for enhancing growth performance and alleviating diarrhea as well as improving intestinal microflora and barrier function of weanling pigs (You et al. 2012). The weaned piglets of 24 to 26 days old were used for the test. The control group was fed with the basal diet; groups 1, 2, and 3 were fed with the basal diet adding 2800 g/t zinc oxide, 800 g/t fat-coated zinc oxide, and 500 g/t nano zinc oxide, respectively. The results showed that the pigs' average daily gain raised 15.3, 9.9, and 14.7 %, the ratio of feed to gain reduced 9.6, 7.5, and 10.3 %, the diarrhea ratio reduced 66.7, 55.6, and 55.6 %, respectively; compared with the control group, all were significant ( $P < 0.05$ ), but groups of 1, 2, and 3 have no significant differences in average daily gain, ratio of feed to gain, and diarrhea ratio ( $P > 0.05$ ) among the zinc oxide, fat-coated zinc oxide, and nano zinc oxide. It implied that the fat-coated and nano zinc oxide were a practicable alternative to high-dosage zinc oxide (Ren et al. 2013)

At present, the Se sources most widely used in feed are sodium selenite, but its toxicity is high and the biological utilization rate is low. Furthermore, it has a prooxidant effect, thus causing adverse effects on animals and environments (Zhu and Jiang 2005). The effects of nano Se on fattening pig meat quality, growth, and antioxidant were explored with sodium selenite as the control. When the level of Se source was 0.4–1.0 mg/kg, then the growth performance of piglets, drip loss, glutathione peroxidase (GSH-Px) activity, T-AOC level, and muscle Se content of the longissimus in the nano Se group were significantly higher than those of the sodium selenite group, while the methane dicarboxylic aldehyde (MDA) and content of active oxygen in the nano Se group

were significantly lower than those of the sodium selenite group (Xia et al. 2005, 2006).

As a fourth-generation trace element additive, nano zinc oxide (nano ZnO) possesses surface effect, volume effect, quantum size effect, and so on. These features provide broad application prospects in the feed industry. Nano ZnO can significantly improve animal production performance and reduce the diarrhea rate of piglets. It can also improve the absorption capacity of livestock and poultry intestines and stomach as well as absorption speed and rate, which greatly reduce ratios of feed to meat and feed to egg, thus reducing the production cost (Zhong and Chen 2005). High zinc diets can prevent diarrhea and improve the production performance of piglets, but when its addition dosage is large, it will lead to adversely affect the environment and the pigs' health. Nano ZnO has a unique advantage of physical and chemical properties, and its required dosage in the feed is lower, but it can achieve the same effects as with a high zinc daily diet. Therefore, it can replace the ordinary Zinc oxide (Pan et al. 2005).

Supplementation of chitosan nanoparticle-loaded copper (CNP-Cu) increased average daily feed intake and average daily gain and decreased feed gain ratio and diarrhea rate, and the optimal supplemental level of chitosan nanoparticles loaded copper was 100 mg/kg ( $P < 0.05$ ). These results suggest that supplemental chitosan nanoparticle-loaded copper has beneficial effects on immune and antioxidant function in weaned pigs, which also can increase growth performance and decrease diarrhea rate. Accordingly, chitosan nanoparticle-loaded copper has a potential to substitute antibiotics (Wang et al. 2011a). An effective DNA vaccine for foot and mouth disease (FMD) virus was prepared using mannosylated chitosan nanoparticles to form the foot and mouth disease VpVAC-VP 1-OmpA complex particles. The immunological evaluation indicated that the 20  $\mu\text{g}$  of DNA vaccine complexed with mannosylated chitosan nanoparticles was found optimum in inducing the immune response in G pig (Nanda et al. 2012).

A certain amount of classical swine fever peptides was adsorbed on calcium phosphate nanoparticles and the adsorption reached 70 %. The calcium phosphate nanoparticles with classical swine fever was used as a vaccine adjuvant; antibody levels of calcium phosphate nanoparticles peptide vaccine group were higher than those of peptide alone group but lower than those of Freund's adjuvant group. The increase of body temperatures postponed 16 h in calcium phosphate nanoparticle peptide vaccine group as compared with peptide alone group. It was showed that calcium phosphate nanoparticles played an adjuvant effect on classical swine fever peptide vaccine to a certain extent (Guo et al. 2012).

The effects of 0.3 % Cu(II)-exchange silicate nanoparticles on the growth performance, bacterium populations, and ammonia concentration in piggery were investigated. The two

dietary treatments were basal diet (control group) and basal diet +0.3 % Cu(II)-exchange silicate nanoparticles. The results indicated that addition of 0.3 % Cu(II)-exchange silicate nanoparticles significantly increased the average daily gain by 12.1 % ( $P < 0.05$ ) and decreased feed/gain by 11.0 % ( $P < 0.05$ ). In feeding trial, ammonia concentration of the trial group during morning, afternoon, and evening decreased by 20.1, 23.1, and 21.2 % ( $P < 0.01$ ) compared to the control group. And, the trial group significantly decreased salmonella and *E. coli* count by 6.0 and 8.0 % ( $P < 0.05$ ) (Zhu et al. 2010b).

Nanotechnologies have broad application in the fields of sterilization. The sterilization rates of nano ZnO to *S. aureus* and *E. coli* were 98.9 and 99.9 % after 5 min of treatment, respectively, which were significantly higher than those of common ZnO (Zu et al. 1999). The inhibition zone diameter to the pathogenic bacteria of nano ZnO was twice that of the common ZnO. Under light conditions, the antibacterial effect of nano ZnO was better (Qu and Jiang 2004). Crystal zinc Bei (nano ZnO, 300 mg/kg) and high-dose ZnO (3000 mg/kg) were used to feed weaned piglets aged 21 days in the early stages. The nano ZnO and high-dose ZnO were all capable of improving the daily gain of piglet, and the nano ZnO group was 27.9 % higher than that of the high zinc group ( $P < 0.05$ ). There were no significant differences in the feed meat ratio and diarrhea rate among various groups ( $P > 0.05$ ). Comparative tests on the effects of added nano ZnO on production performance were conducted. Seventy-five piglets were divided into five groups, among which the fourth group was the high zinc group (Zn 3000 mg/kg), the fifth group (control group) was the normal zinc group (Zn 100 mg/kg), and the other three were “crystal zinc Bei” groups (group 1 with the addition of 250 mg/kg, group 2 with 375 mg/kg, group 3 with 500 mg/kg). The high zinc group and different concentrations of nano ZnO groups both could improve the daily gain of piglets. Compared with that of the normal zinc group, the weight of the high zinc group was increased by 13.5 %. The three concentrations of nano ZnO groups (with the addition nano ZnO of 250, 375, and 500 mg/kg) were respectively increased by 9.9, 18.1, and 11.6 %. The high zinc group and nano ZnO group could both decrease the ratio of feed and meat ( $P > 0.05$ ). In respect to piglet diarrhea, the nano ZnO groups were significantly better than the normal zinc group ( $P < 0.05$ ), of which the high zinc group reduced by 28.2 %, and nano ZnO groups respectively decreased by 19.5, 23.9, and 26.4 %. The nano ZnO groups and high zinc group showed good effects on the piglets’ daily weight gain, feed meat conversion ratio, and reduction rate of diarrhea, among which the 375 mg/kg nano ZnO group had the best effect on weight gain. However, with the increasing dose of nano ZnO, the diarrhea reduction rate effects on piglets showed a decreasing trend (Wang et al. 2003).

The water and feedstuff were treated with nano-863 and to feed pigs, the pigs’ tempers were stable, their daily weight gain was 9.2 % higher than that of the conventional feed group (control), and the feed to gain ratio was decreased by 3.0 %. As the color of pigs’ hair is also more pleasant, the price of the treated pigs is 0.20 ¥/kg higher than that of the control due to the improvement of the meat. Under the same treatment, the daily weight gain of pigs on a pig breeding farm was 113 g higher than that of the control group (increased by 17.3 %). The feed to gain ratio was decreased by 7.8 %. In addition, the cost of feed was reduced by 0.28 ¥ (7.6 %). The pigs in the test group liked to eat and sleep, their hair color was more lustrous, skin was ruddy, and fecal odor was reduced.

Montmorillonite disinfectant is produced by adsorption and ion exchange reaction among copper salt, iron salt solution, and nano montmorillonite. As calculated by weight percentage, the contents of copper and iron in montmorillonite were 1.5–6.5 %, in which the weight ratio between copper and iron was 1:0.25–0.50. The disinfectant has broad-spectrum antimicrobial function, durable effectiveness, preventing drug resistance, low production cost, safe operation, and an environment-deodorizing function; thus, it can effectively improve the economic benefits of breeding industry. It can be used for the disinfection of livestock, poultry, and hatching eggs, and their cultivation places and facilities.

The composite plastic film which contains Nano TiO<sub>2</sub> (1 % TiO<sub>2</sub> concentration) was used as an antibacterial agent. The sterilization rate on *E. coli* and *S. aureus*, and *Bacillus subtilis* var. reached 99.9 and 97.4 % after treating 24 h, respectively. TiO<sub>2</sub>/SiO<sub>2</sub> composite particles exhibited a stronger antibacterial performance. The nano composite materials showed obvious sterilizing effect used for object surface treating agent even under low and normal lighting conditions, which provides the possibility for application of nano composite materials in animal breeding (Li et al. 2001). The resistance effects of new nano inorganic antimicrobial agent nano TiO<sub>2</sub> and nano ZnO on several pathogenic organisms were investigated. The test results on *E. coli*, *S. aureus*, *B. subtilis*, *C. albicans*, and *Aspergillus niger* demonstrated that the new nano TiO<sub>2</sub> and nano ZnO had high efficiency and broad-spectrum antibacterial ability and showed strong inhibitory effects on *E. coli*, *S. aureus*, *B. subtilis*, and *C. albicans*. The mass fraction concentration of  $75 \times 10^{-6}$  nano TiO<sub>2</sub> and nano ZnO inhibited and killed more than 99 % of *E. coli*, *S. aureus*, and *C. albicans* and more than 90 % of *B. subtilis*, the antibacterial ability of which on *A. niger* is stronger than the similar Japanese antibacterial agent AG300 and phenol. This indicates that the nano TiO<sub>2</sub> and nano ZnO antibacterial agents have strong inhibition and bacteria-killing abilities as well as efficient broad-spectrum antibacterial properties against gram-positive and gram-negative bacteria, bacillus, yeasts and

molds, and other different types of bacteria (fungi) (Long et al. 2007).

#### 4 Application of nanotechnologies in aquaculture

Nanotechnologies have broad application in fishery industry, such as water treatment, fishpond sterilization, nano feed for feeding the fish, and controlling of aquatic diseases.

##### 4.1 Nanotechnologies and fishery industry

Nanoparticles of elements like selenium, iron, etc. sources supplemented in diet could improve the growth of fish. The technology can be applied for using in aquariums and commercial fish ponds to reduce the cost of water treatment. Researchers believe that nanotechnologies may have the potential to provide fishponds that are safe from disease and pollution. Another application possibility of nanotechnologies is the usage of different conservation and packaging techniques to provide seafood safety by delaying mildew and microbial spoilage (Can et al. 2011). Nano TiO<sub>2</sub> could achieve desirable sterilization efficiency on three bacteria of *E. coli*, *Aeromonas hydrophila*, and *Vibrio anguillarum*. In ultraviolet lights, 0.1 g/L nano TiO<sub>2</sub> could reach a sterilizing rate above 98 % after 2 h and it could still keep a sterilizing rate above 96 % after 2 h in the sun. The photocatalytic sterilization efficiency of nano TiO<sub>2</sub> was correlative with its concentration and reaction time. Without adequate concentration or reaction time, the sterilization would not be effective (Huang et al. 2010).

Nanotechnologies were widely used for water treating and breeding fish. The application of nanotechnologies in seawater shrimp aquaculture revealed that the nano device was capable of improving water quality, reducing the rate of water exchange, and improving shrimp survival rate and yield (Wen et al. 2003). Among several nano devices, nano net treatment was the best; the results showed a 100 % increase in survival rate of fish, while water nitrite and nitrate both decreased, with nitrite decreasing to as low as one fourth of the control group. Nanotechnologies also increased the water pH, and the water quality was improved significantly. It has shown a broad prospect in aquaculture (Liu et al. 2008b).

Another experiment of nano-863-treated water and breeding fish were performed; the effects on the quality of water were investigated. Without changing the water for 6 months, the contents of NH<sub>3</sub>-N, NO<sub>2</sub>-N, NO<sub>3</sub>-N, and CD in the test groups were 0.58, 0.13, 0.89, and 8.95, respectively, all of which were lower than those of the control group with conventional water changing, i.e., 1.58, 0.28, 2.33, and 19.22. The pH value of the experimental group was 7.20, which was higher than that of the control group (5.60), indicating that nano-863 can improve water quality and is more conducive to

the growth of fishes. Nano-863 was also used in shrimp farming in fisheries aquatic breeding farm. One million tailed shrimps were included in each of the experimental and control groups. Seven hundred thirty thousand tailed shrimps survived in the test group, while only 360 thousand survived in the control group; thus, the survival rate of the test group is twice that of the control group. Nano-863 can also enhance the activity and energy of water, enhance shrimp appetite, and promote growth and development; it also has very strong antibacterial and algae and disease protection efficacy.

The basal fish bait was used as the control, and different doses of sodium selenite, selenomethionine, and nano Se were added, to investigate the effects of Nile tilapia (*Oreochromis niloticus*) on growth performance. Regardless of the form of Se, low doses of Se (0.1 mg/kg) in feed had a growth-promoting effect on fish, but the effect was not significant ( $P > 0.05$ ), while moderate doses of Se (0.5 mg/kg) in feed had a significant promoting effect on the growth of fish ( $P < 0.05$ ). However, there was no dramatic difference between the three selenium sources of sodium selenite, selenomethionine, and nano Se ( $P > 0.05$ ). When high doses of Se were placed in the feed (2.5 mg/kg), the effects of different Se sources on the growth performance of fish were different. High doses of sodium selenite induced no significant weight gain of fish in comparison with the control group ( $P > 0.05$ ). However, high doses of nano Se had obvious promoting effects on the growth of fish. The Nile tilapia weight gain rate was  $86.3 \pm 4.7$  %, which was higher than that of the control group ( $51.9 \pm 4.8$  %) (Deng and Chen 2003).

##### 4.2 Nanotechnologies in controlling of aquatic diseases

The aquaculture industry has suffered tremendous losses due to disease caused by bacteria (Huang et al. 2010). At present, traditional disinfection and sterilization methods are mostly used to control aquatic diseases, and various chemical disinfectants, antibiotics, and sulfa drugs are frequently used in large quantities. The cost of these chemical drugs is quite high, stimulation is strong, efficiency is low, and there are numerous side effects; thus, various related problems cannot be fundamentally solved, leading in turn to many adverse effects (Yang 2003).

Not only is nano TiO<sub>2</sub> able to degrade the organic pollutants in water, but it also has the abilities of sterilization and disinfection. Under ultraviolet irradiation conditions, nano TiO<sub>2</sub> can produce highly active hydroxyl -OH, superoxide ion -O<sup>-</sup>, peroxy radical -OOH, and other free radicals with high oxidation capacity. These free radicals can interact with biomacromolecules, such as lipids, proteins, enzymes, and nucleic acid molecules in bacteria, viruses, and other microorganisms, which can destroy cell structures through a series of chain reactions so as to achieve the effects of sterilization and disinfection by protein denaturation and lipolysis of

bacteria, and their sterilization efficiency is much higher than that of traditional bactericide (Yu et al. 2002; Sonawane et al. 2003; Zhao et al. 2000). In natural environments, nano TiO<sub>2</sub> shows strong sterilization effects only in the presence of sunlight. The catalytic effect of sunlight is similar to ultraviolet without the need for additional use of artificial light, which is conducive to the promotion and application of the technology in aquaculture industry.

The harmful and beneficial bacteria in aquaculture were detected by using copper-bearing montmorillonite (Cu<sup>2+</sup>-MMT) nanotechnologies (Liu et al. 2009c). The detected harmful bacteria were the aquatic animal intestinal pathogenic bacteria *Aeromonas hydrophila*, *Vibrio parahaemolyticus*, and *Pseudomonas fluorescens*. Probiotics were the intestinal *Lactobacillus acidophilus* and *B. subtilis* which isolated from silver carp and grass carp. The minimum inhibitory concentrations of copper-bearing montmorillonite on *A. hydrophila* and *P. fluorescens* were both 128 µg/mL. The minimum bactericidal concentrations were both 512 µg/mL. The minimum inhibitory concentration on *V. parahaemolyticus* was 64 µg/mL, and minimum bactericidal concentration was 256 µg/mL. The minimum inhibitory concentrations of copper-bearing montmorillonite on *Bacillus* and *L. acidophilus* were both 1024 µg/mL, and minimum bactericidal concentrations all were more than 1024 µg/mL. The above results indicated that copper-bearing montmorillonite showed strong antibacterial and bactericidal effects on the three aquatic pathogenic bacteria. Furthermore, the minimum inhibitory concentrations and minimum bactericidal concentrations of *V. parahaemolyticus* on copper-bearing montmorillonite were less than those of *A. hydrophila* and *P. fluorescens*, which demonstrated higher sensitivity and larger values of minimum inhibitory concentrations and minimum bactericidal concentrations on bacteria, illustrating that their influence was small.

## 5 Development of new type of nanotechnologies pesticides and plant protection

To develop new types of chemical pesticides and biological pesticides or dilute the pesticides with the water that was treated with nanotechnologies for spraying, all could improve the properties and control efficiency of pesticides. The insecticidal efficacy of nano biopesticide is threefold of the ordinary pesticides, and the cost of production is half of ordinary pesticides (Gao 2006).

### 5.1 Development of new type of nano pesticides

Jinggangmycin nanocapsules with Jinggangmycin as the core material were prepared by micro-emulsion polymerization.

**Table 3** Indoor test results of controlling the pests of nano-biopesticide and no-nano-biopesticide

Contents	No-nano-biopesticide	Nano-biopesticide
Active ingredients content	40 %	18 %
Dilution ratio of pesticide	800	1500
Control efficiency (average)	56 %	98 %

Against rice sheath blight pathogen (*Rhizoctonia solani*), indoor virulence test results showed that the half effect concentration value (EC<sub>50</sub>) of Jinggangmycin nanocapsule was 4.23 µg/mL, with an efficacy 88-fold over the original drug. Field experiments showed that the control efficacy of Jinggangmycin nanocapsules was 1.2 times the original for the same concentration of 5 µg/mL (Lin et al. 2014).

The amphiphilic graft copolymers are the main composition of the nanocapsules and used widely in the drug areas, such as improving the performance of conventional agrochemicals and increasing the control efficiency (Li et al. 2011a). The synthesis and screening processes of nano biological pesticides were completed in 2003 by different units in China, and both indoor and field tests have achieved ideal results. A production line with an annual production scale of 200 t has also been built. The insecticidal efficacy and comprehensive properties of biological pesticide after nano treatment have been greatly improved (Table 3). Indoor testing results showed that the tested insects mortality were 100 % after treatments of dilution 1500-time nano biological pesticide, and the tested insects mortality of dilution 4000-time were 96.4 %. Field test for controlling the insect pests was carried out; the tested insect pests mortality of dilution 1500-time after performing 24 and 48 h were more than 90 and 98.5 %, respectively (Table 3).

### 5.2 Pesticides dilution with nanotechnologies treated water

Nano-863-treated water was then used to dilute pesticide for spraying; the treated leaves of plant in the treatment group were tender and green and did not turn yellow in the cold weather. The disease-resistant and cold-resistant effects were significant enhanced and show no appearance of blight. The evident yield-increasing effects were also achieved in balsam pear, pepper, corn, and other crops. After the nano-863-treated water was applied, the crop root system was well developed, drought resistance was significantly improved, and lodging-resistant ability was increased. It was also found that carbon nanotubes may promote the absorption of moisture by tomato seeds, thus improving the seed germination rate and promoting growth (Khodakovskaya et al. 2009).

### 5.3 Nanotechnologies in inhibition of pathogens

**Effect of nanotechnologies on plant pathogens** Two types of inorganic material SiO<sub>2</sub>, namely, nanoparticle material A (100 nm diameter) and nanoparticle material B (60 nm diameter), were artificially synthesized through the simulation of biological SiO<sub>2</sub>, the inhibitory effect of which on wheat powdery mildew (*Blumeria graminis*) was examined in the laboratory. The inhibitory effect of nanoparticle material A was 61 %, and that of nanoparticle material B was more than 80 %, which was significantly higher than that of the common inorganic silicate (Wang et al. 2001). The modification of plant leaf surface by using nanostructured silica sphere may alter the original topology structure and hydrophobic properties of plant leaf surface and form a special amphiphilic surface, which in turn affects the fungal extracellular matrix release, blocks the first step reaction of the high specificity of the supramolecular recognition process of fungal spores and surface of host, and changes the early infection process, so as to determine the control measures of the targeted fungal disease.

The effects of nano silver (Ag) on the toxicity to 14 plant pathogens were explored by using the indoor toxicity determination method. The silver nanoparticle could significantly inhibit the fungal hyphal growth of the sheath blight pathogen (*R. solani*), *Colletotrichum musae*, and the other ten types of fungi. The EC<sub>50</sub> ranged between 2.7267 and 36.2465 µg/mL. The virulence on the inhibition of mycelium growth of *R. solani* and banana anthracnose pathogens was strong, with EC<sub>50</sub> of 2.7267 and 3.8871 µg/mL, respectively. The nano silver showed strong inhibitory effects on the spore germination of nine types of plant pathogenic fungi, including banana *Colletotrichum graminicola*, and the EC<sub>50</sub> was 0.0275–1.0927 µg/mL, in which the virulence of inhibition of rice blast fungus (*Magnaporthe oryzae*) spore germination was the strongest (EC<sub>50</sub> was 0.0275 µg/mL). For the same pathogen, the inhibition effect of nano silver on spore germination was significantly greater than that of inhibiting mycelial growth. The nano silver with concentration of 2.5–40 µg/mL was used to treat kenaf *B. cinerea*, citrus *Penicillium digitatum*, and tobacco *Sclerotium rolfsii* for 48 h; the mycelia growth inhibition rate were only 20–40 %; and the nano silver dose and mycelial growth inhibition rate showed no linear relationship (Liu and Xu 2008).

The possible inhibition mechanisms of nano silver on the growth of plant pathogens are as follows. Silver nanoparticle can lead to that mycelial respiration becomes weak and increases cell membrane permeability. The respiratory oxygen consumption amount of the suspended mycelium liquid was significantly lower than that of the control hyphae after nano Ag treatment. In a dose of 9 µg/mL nano silver treating for 2 h, the oxygen breathing inhibition rates on rice blast fungus *M. oryzae* and Chinese cabbage black spot disease

*Alternaria brassicae* were 57.7 and 63.1 %, respectively. Suspended mycelium treated with nano silver, the mycelium liquid conductivity value was significantly higher than that of the control. The conductivity showed a gradual increasing trend with the extension of the treatment time. Nano silver treated for 2 h, the conductivity of mycelium suspension was twice that of the control, and microscopic observation showed that twist, expansion, cell collapse, wilting, and apoptosis of mycelium cell were present. A 60 µg/mL concentration of nano silver was used to treat rice leaves in vitro, which demonstrated a certain preventive effect against *M. oryzae*, and the relative control effect reached 72.2 %. The control effect was improved with the increase of drug concentration. The control effect was represented by a less lesion numbers and smaller lesion size.

### 5.4 Nanotechnology application in plant protection

Nanotechnology approaches on plants allow more efficient and sustainable food production by reducing the chances of disease and pest incidence in plants (Nair and Kumar 2013). Historically, various fields, such as medicine, environmental science, and food processing, have employed the successful and safe use of nanotechnologies. However, their use in agriculture, especially for plant protection and crop production, is currently an under-explored area in the research community. Preliminary studies show the potential of nanotechnologies in improving seed germination and growth, plant protection, pathogen detection, and pesticide/herbicide residue detection (Khot et al. 2012).

The development of nanotechnology in conjunction with biotechnology has significantly expanded the application domain of nanotechnologies in various fields. In addition, a variety of carbon-based, metal- and metal oxide-based dendrimers (nano-sized polymers), and bio-composites nanomaterials (Environment Protection Agency, EPA 2007; Nair et al. 2010) are currently being developed. Their types include single-walled and multi-walled carbon nanotubes (SWCNT/MWCNT), such as nanoparticle of magnetized iron, aluminum, copper, gold, silver, silica, zinc and zinc oxide, titanium dioxide, cerium oxide (Ce<sub>2</sub>O<sub>3</sub>), etc. General applications of these materials are found in water purification, wastewater treatment, environmental remediation, food processing and packaging, industrial and household purposes, medicine, and smart sensor development (Jain 2005; Wei et al. 2007; Byrappa et al. 2008; Zhang and Webster 2009; Gao and Xu 2009; Qureshi et al. 2009; Lee et al. 2010; Zambrano-Zaragoza et al. 2011; Bradley et al. 2011). The majority of applications in these areas have focused on the significance of the nanotechnologies for improving efficiency and productivity. These materials are also used in agriculture production and crop protection (Bouwmeester et al. 2009; Nair et al. 2010; Sharon et al. 2010; Emamifar et al. 2010).

### 5.5 Nanotechnologies on microorganisms and insects

**Nanotechnologies and plant pathogens** The inhibitory effects of nano CuO (average diameter 20 nm), 50 % carbendazim wettabile powder (WP), and 75 % chlorothalonil WP on tomato early blight *Alternaria solani*, pepper root rot bacteria, *Fusarium oxysporum*, and vegetable *B. cinerea* were tested in laboratory (Dong and Yang 2011). The inhibition efficiency of the 500–750 mg/kg nano CuO against tomato early blight *A. solani* was 70.7–81.7 %, while that of 750 mg/kg nano CuO against *F. oxysporum* was 84.0–89.0 %, both of which were significantly better than those of the 50 % carbendazim and 75 % chlorothalonil. The inhibitory effect of the 500 mg/kg nano CuO on pepper root rot pathogen was significantly lower than that of the 75 % chlorothalonil, but higher than that of the 50 % carbendazim. The antibacterial effects of the 50 % carbendazim and 75 % chlorothalonil on vegetable *B. cinerea* reached 88.6 and 93.2 %, respectively. However, the nano CuO showed no inhibitory effect on vegetable *B. cinerea* (Table 4).

**Effects of nanotechnologies on bacteria** The toxicities of nanotechnologies to bacteria growth were investigated. The *E. coli*, *B. subtilis*, and *Agrobacterium tumefaciens* were exposed to nano-Au, nano-Ag, nano-Fe, and fullerene (C<sub>60</sub>). As an effective bactericide, nano-Ag induced high toxicity on these three bacteria, and C<sub>60</sub> inhibited their growth, but *B. subtilis* and *E. coli* recovered as exposure time extended. Nano-Au and nano-Fe had hardly any effect on the three bacteria. *A. tumefaciens* showed the lowest resistance and slowest growth rate during exposure. Images obtained by scanning electron microscope (SEM) revealed that nano-Ag could cause damage to the cell structure of the three bacteria at 1 µg/mL. Slight damage on *E. coli* was found when exposed to C<sub>60</sub>, whereas no obvious

physical damage was found after exposure to nano-Au or nano-Fe. It is assumed that the surface activities of nano materials may be responsible for the different toxic effects on these bacteria (Wang et al. 2012c).

The germicidal effects of nano-copper-bearing montmorillonite on *A. hudrophila*, *V. parahaemolyticus*, and *P. fluorescens* increased with the concentration, and the effects on *L. acidophilus* and *B. subtilis* also somewhat increased, but to a lower extent. Nano-copper-bearing montmorillonite showed a stronger bactericidal performance at 30 °C than at 4 °C. The bactericidal efficiency was 100 % in *A. hudrophila*, *V. parahaemolyticus*, and *P. fluorescens*, 24.9 % in *L. acidophilus*, and 25.6 % in *B. subtilis* after 12-h bacterial culture at 30 °C, respectively. However, at 4 °C, the bactericidal efficiency was 83.9, 84.8, 84.6, 20.9, and 21.4 %, respectively, after 24-h bacterial culture (Liu et al. 2009c).

**Control efficiency of nano SiO<sub>2</sub> on fungi and fungal diseases** Silicon (Si) is one of the most abundant elements in nature. The Si element can self-assemble into bio-mineralized nano SiO<sub>2</sub> in plants, thus reducing the occurrence of plant fungal diseases (Wang et al. 2001). The resistance effect of Si on leaves of two rice varieties with nano SiO<sub>2</sub> inoculation treatment against *Magnaporthe grisea* was investigated. The resistant variety Nongda 18 and susceptible variety Mongolian rice to *M. grisea* were observed by means of scanning electron microscope and transmission electron microscopy (TEM) and compared with control groups without the SiO<sub>2</sub> treatment. The findings showed there were only a few hyphae of *M. grisea* on both leaves and fewer hypha quantities than the control group without Si treatment. Based on the transmission electron microscopy images, it was clearly observed that Si may prevent the hypha from penetration by enclosing the hypha around the sites penetrated. The results indicated that the nano SiO<sub>2</sub> were able to protect the rice from the pathogenic fungus

**Table 4** Antibacterial effect of nano-CuO and other fungicides on various vegetable disease pathogens

Treatments	Concentration (mg/kg)	<i>Alternaria solani</i>				<i>Fusarium oxysporum</i>				<i>Botrytis cinerea</i>			
		96 h		168 h		96 h		168 h		96 h		168 h	
		Dia.* (mm)	Contro. E.*(%)	Dia. (mm)	Contro. E. (%)	Dia. (mm)	Contro. E. (%)	Dia. (mm)	Contro. E. (%)	Dia. (mm)	Contro. E. (%)	Dia. (mm)	Contro. E. (%)
50 % carbendazim	1250	38	36.67E	49	40.24D	25	50.00D	40	45.21D	3	92.50A	5	88.64B
75 % chlorothalonil	1250	28	53.33C	40	51.22C	19	62.00B	22	69.86B	3	92.50A	3	93.18A
Nano-CuO	750	12	80.00A	15	81.71A	8	84.00A	8	89.04A	38	5.00B	44	0.00C
	500	17	71.67B	24	70.73B	22	56.00C	24	67.12C	38	5.00B	45	-2.27C
	250	32	46.67D	48	41.46D	44	12.00E	58	20.55E	40	0.00C	45	-2.27C
Sterile water (control)	/	60	0.00 F	82	0.00E	50	0.00 F	73	0.00 F	40	0.00C	44	0.00C

The numbers in the same column with different capital letters represent significantly different at 1 % level by using Data Processing System (Tang 2013) analysis and Duncan's multiple comparison

Dia. diameter, Contro. E. control efficiency

(Liu et al. 2012a). It was also shown that the disease indexes of Nongda 18 and Mongolian rice with nano SiO<sub>2</sub> treatment respectively decreased by 31.0 and 51.0 % compared with those without Si processing. The relative control effect of disease-resistance varieties reached 54.9 %, while the susceptible varieties reached 73.5 %. The silicon application reduced the disease level and index and strengthened the resistance to rice blast, particularly among the susceptible Mongolian rice. Nano-silica application to rice can not only significantly improve the content of chlorophyll, net photosynthetic rate, stomatal conductance, and intercellular carbon dioxide concentration, which help to enhance the photosynthesis of rice leaf, but it can also increase the number of new roots and their longest length and improve the active absorption area and vigor of roots. At the same time, it can also increase the contact angle of rice leaves and reduce the leaf angle and attachment of fungi (Liu et al. 2012b).

*Nano silver-silicon on inhibition of a variety of fungi and bacteria* The nanosized silica-silver (NSS) was developed, which consisted of nano-silver combined with silica molecules and water-soluble polymer and prepared by exposing a solution including silver salt, silicate, and water-soluble polymer to radioactive rays. In addition, the antifungal and antibacterial effects of nanosized silica-silver and antifungal effect on powdery mildew and chemical injuries from nanosized silica-silver at high concentrations on plants were tested. The control effects of the nanosized silica-silver on pathogenic fungi of plants infected with powdery mildew were carried out in field and green house (Park et al. 2006). The results showed that the nanosized silica-silver antifungal activity was against the tested phytopathogenic fungi at 3.0 ppm with varied degrees. In contrast, a number of beneficial bacteria or plant pathogenic bacteria were not significantly affected at the 10-ppm level, but completely inhibited by 100 ppm of nanosized silica-silver. Among the tested plant pathogenic

fungi, the new product effectively controlled powdery mildews of pumpkin at 0.3 ppm in both the field and greenhouse tests. The pathogens disappeared from the infected leaves 3 days after spraying, and the plants remained healthy thereafter. This suggests that the nanosized silica-silver was effective in controlling various plant fungal diseases, as shown in Table 5.

Furthermore, the nanosized silica-silver inhibited spore germination of *B. cinerea* at a low concentration of 3 ppm. In the non-treatments, 10 % spore germination occurred after 5 h, whereas in nanosized silica-silver treatments, any spores were not germinated until 10 days. The 3.0 ppm of nanosized silica-silver effectively inhibited several tested pathogenic fungi with varied degrees, while some fungi were effectively suppressed even at 0.3 ppm. However, most bacteria, either useful or plant pathogenic, were not suppressed at 10 ppm, but strongly inhibited at 100 ppm (Table 5).

The chemical injuries on plants due to application of nanosized silica-silver were tested. An undiluted solution and diluted 10, 100, and 1000 times of nanosized silica-silver were sprayed on the surfaces of crops leaves, including new leaves of cucumber and pansy; chemical injuries on plants were observed after 3 days. Compared to the control group (sprayed pure water), typical chemical injury phenomena, such as wrinkles of new leaves, did not appear in the treatment groups using the diluted solutions (3.2–3200 ppm). Any phytotoxic phenomena were not detected in the solution applied to plants. The results were the same as when applied to other plants (Park et al. 2006).

The smaller the size of nano silver, the more effectively fungal growth was suppressed. In general, 1- to 5-nm-sized particles may pass through a protoplasm membrane, and silica is well absorbed into fungi (Wainwright et al. 1986). When the nanosized silica-silver is absorbed into fungal cells, silver nanoparticles function to increase disinfecting activity. Silica, which induces dynamic resistance to diseases to

**Table 5** Effective concentration of nanosized silica-silver on suppression of microbial growth

Microorganisms	Growth inhibition (%) according to concentration of the nanosized silica-silver			
	0.3 ppm	3.0 ppm	10 ppm	100 ppm
<i>Pythium ultimum</i>	15.5	66.7	100	100
<i>Magnaporthe grisea</i>	1.4	27.0	100	100
<i>Colletotrichum gloeosporioides</i>	11.8	21.6	100	100
<i>Botrytis cinerea</i>	2.6	82.7	100	100
<i>Rhizoctonia solani</i>	54.8	94.8	100	100
<i>Bacillus subtilis</i>	0	0	50.0	100
<i>Azotobacter chroococcum</i>	0	0	0	100
<i>Rhizobium tropici</i>	0	0	0	100
<i>Pseudomonas syringae</i>	0	0	0	100
<i>Xanthomonas campestris</i> pv. <i>vesicatoria</i>	0	0	0	100

increase resistance, acts to form a physical barrier to pathogenic fungi (Kim et al. 2002). Thus the recurrence of diseases may be prevented for a considerably long period after disinfection of pathogenic microorganisms. The results showed that the nanosized silica-silver product is effective in controlling various diseases at lower than 3.0 ppm, which is not a concentration that may suppress pathogens on agar medium. The following plant pathogenic fungi may be treated and controlled using the nanosized silica-silver: *Blumeria spp.*, *Sphaerotheca spp.*, *Phytophthora spp.*, *Rhizoctonia spp.*, *Colletotrichum spp.*, *Botrytis spp.*, *Magnaporthe spp.*, and *Pythium spp.* In addition, the composition for controlling plant pathogens may control pathogenic bacteria in plants at a concentration higher than 10 ppm.

Nanosized silica-silver exhibits a wide range of antimicrobial activity and can control both spores germination and hyphae growth of fungus. In addition, the nanosized silica-silver manifests efficient controlling effects at low concentrations and may maintain the controlling effects for a long period after a single application. Furthermore, the nanosized silica-silver does not cause chemical injuries and is non-toxic to the human body (O'Neill et al. 2003) as well as plants, even with a high concentration. It was found that the nanosized silica-silver's character provides a composition for controlling pathogenic pathogens in plants. The nanosized silica-silver can selectively control the microorganisms depending on its concentration. Due to the fact that Ag and SiO<sub>2</sub> are known to be environmentally safe and even beneficial for human health (Shankar et al. 2003; Yao et al. 2004) and the cost of nanosized silica-silver is much lower than commercial fungicides, it is believed that the formulation is highly useful to manage various fungal plant diseases in ecofriendly sustainable agriculture.

*The results showed that the nanosized silica-silver antifungal activity* The single-step "green synthesis" protocol for the production of Au nanoparticles utilizing culture filtrate of a phytopathogenic fungus *Alternaria alternata* was established, and Au nanoparticles were synthesized by bio-reduction of chloroauric acid (HAuCl<sub>4</sub>) using the fungal culture filtrate of *A. alternata*. In addition, treatment of the fungal culture filtrate with aqueous Au<sup>+</sup> ions produced Au nanoparticles with an average particle size of 12±5 nm (Sarkar et al. 2012). *Cochliobolus lunatus* was used to produce Ag nanoparticles for insecticide in killing mosquito larva with clean, nontoxic, and environmentally acceptable metal nanoparticle; the silver nanoparticles which are formed are hydrophilic in nature, disperse uniformly in water, are highly stable, and have significant mosquito larvicidal activity against *Aedes aegypti* (Linnaeus, 1762) and *Anopheles stephensi* Liston (Diptera; Culicidae). Furthermore, the nanoparticle has no toxicity toward non-target organisms and beneficial organisms. Toxicity studies carried out against the non-target fish species

*Poecilia reticulata*, the most common organism in the habitats of *A. aegypti* and *A. stephensi*, showed no toxicity at LC<sub>50</sub> and LC<sub>90</sub> doses of the Ag nanoparticles (Salunkhe et al. 2011).

Nanotechnologies can be used for rice bacterial leaf blight pathogen *Xanthomonas campestris* pv. *oryzae* (Xoo) strain detection. The nano silver film was prepared by the electrolysis method using silver nitrate and polyvinyl alcohol, the glass slides were placed in the electrolyte, and the nano silver film was formed. The surface-enhancing Raman spectrometers of seven *X. campestris* pv. *oryzae* "physiological races" on silver film were examined by using a portable Raman spectrometer. There were many differences in the peak positions and relative intensity of the peaks of surface enhancing Raman spectrometers spectrum of the seven physiological races, which puts forward a new method for the fast and convenient detection of different physiological races of *X. campestris* pv. *oryzae* (Kang et al. 2010). Gene vectors of diameter less than 10-nm magnetic nanoparticles were synthesized through nanoparticles absorbed green fluorescent protein. The nanoparticle gene vector can be transferred into plant cells by electroporation and can be used in the research of genetic transformation (Wang et al. 2010a).

## 6 Nano fertilizers and effects on crops

Nano fertilizer is a branch of nanotechnologies and is a new fertilizer produced by using nanoparticles construction, medicine microcapsule technology, and chemical micro emulsion technology modifications, including nano structure fertilizer and nanoparticle-coated fertilizer, or cemented slow/controlled release fertilizers (Zhang et al. 2002).

### 6.1 Effects of nano fertilizer on rice crop

Comparing with the normal urea treatments, the tiller numbers, SPAD values, and accumulation amounts of dry matter are increased significantly under the nanometer urea treatments with the same nitrogen rate. Meanwhile, the grain yields of the nanometer urea treatments are larger than those of the normal urea treatments when the nitrogen rates are from 0 to 90 kg/ha, while the grain yields and agronomic efficiency of nitrogen fertilizer of the nanometer urea treatments are increased significantly when the nitrogen rates are further increased, and the grain yield is increased by 10.2 % and agronomic efficiency of nitrogen fertilizer is increased by 44.5 % in their maxima. Based on the developed model between the yield and the fertilizer rate, the agronomic efficiencies of the normal urea are only 58.3–87.6 % of those of the nanometer urea when the nitrogen rates are from 90 to 244.9 kg/hm<sup>2</sup> and the nanometer urea can save 12.4–41.7 %



of nitrogen. It is suggested that the nanometer urea treatment with N 244.9 kg/hm<sup>2</sup> is the perfect treatment for high-grain-yield cultivation and has the highest grain yield of 11,174.7 kg/hm<sup>2</sup> and a much higher agronomic efficiency of nitrogen fertilizer, and the nanometer urea treatment with N 180 kg/hm<sup>2</sup> is the perfect treatment for safe cultivation and has much higher grain yield and agronomic efficiency of nitrogen fertilizer (Wang et al. 2010c). The same results were obtained by others experiments (Wang et al. 2011d; Li 2013).

Hybrid rice is very important in China rice production, the current growth area of hybrid rice account for more than 56 % of rice planting area in China (Yuan 2014). Compared with the normal synergistic fertilizer of 100 % efficient fertilization, the nano-synergistic fertilizer had obvious yield-increasing effect on hybrid rice. The nano-synergistic fertilizer could increase the yield by 4.4–10.4 % with 60 % fertilization, 9.5–21.1 % with 70 % fertilization, and 4.7–15.8 % with 100 % fertilization. So, the nano-synergistic fertilizer could reduce the amount of fertilizer 30–40 % and has obvious yield-increasing effect. The mechanism of nano-synergistic fertilizer on hybrid rice showed that nano carbon mixed with water became the superconductor, which increased the electric potential of soil. The nano carbon soil made the soil colloid recombinant and release large amounts of nutrient elements. The nano-synergistic fertilizer made the outflow quantity of NH<sub>4</sub> reduce in hybrid rice root, increase the absorption quantity of NO<sub>3</sub><sup>-</sup>, and promote the absorption of nitrogen ion in root system on soil (Zhang et al. 2012).

Nano fertilizer also can promote the growth and increase the yield of rice. The survey results of yields in various treatment groups displayed the following trends: 100 % nano fertilizer treatment > 100 % conventional fertilization treatment > 70 % nitrogen amount of nano fertilization treatment > 70 % total nano fertilization treatment > 70 % nitrogen amount of conventional fertilization treatment > 70 % total conventional fertilization treatment > no nitrogen fertilizer + nano fertilizer > nano fertilizer > no nitrogen fertilizer > blank control. With the same amounts of phosphorus and potassium fertilizer, the nitrogen use efficiency of the 70 % nitrogen nano fertilization treatment was shown to be 11.6 % higher than that of the conventional fertilization. The yield of single application nano fertilizer treatment was 32.3 % higher than that of the blank control, indicating that the nano fertilizer promoted the growth of rice (Zhang et al. 2010).

Total nitrogen concentration increased sharply after nano urea fertilizer application. At the same nitrogen rate, the total nitrogen concentration in the nano urea treatments decreased significantly faster than those of the common urea (control). The safe drainage water time was 11.5–15.9 days after nano urea application whereas 12.5–17.3 days after common urea application, it means that the nano urea

is easier and quickly absorbed than common urea. N loss in nano urea treatment was 70.6–74.3 % of N loss in control treatments. Rice grain yield and N agronomic efficiency of nano urea treatments were higher than those of the control. Of the nano urea N, 225 kg/hm<sup>2</sup> was recommended as the best rate for achieving high-yield, high-N efficiency, and safe cultivation technique in hybrid rice production (Wang et al. 2011c).

## 6.2 Effects of nano fertilizer on other crops

Nano-carbon was proved to be non-toxic materials. When 5 to 50 nm of carbon was added to the fertilizer, nano-fertilizer was formed. The experiments of nano-fertilizer efficiency on radish, cabbage, eggplant, pepper, tomato, celery, and leek crops were carried out. The results indicated that the nano-fertilizer promoted the growth of the crops and made the yield increase 20 to 40 %, and the vegetables come into the market 5 to 7 days ahead of time. After fertilization the radish grew to 83 cm in 38 days, eggplant reached 1.2 kg in 20 days and so on. Nano-fertilizer also could improve the quality of the vegetables; the content of vitamin C in chili increased 1.5 times (Liu et al. 2009b).

Compared to common fertilizer, the nano-synergistic fertilizer increased the rice yield of 10.3 %, the spring maize of 10.9–16.7 %, the soybean of 28.8 %, and increased the soybean oil content of 13.2 %, and had important significance of cultivating non-genetically modified soybeans. The nano-synergistic fertilizer also had the function of promoting the maize precocity. The input-output ratio of nano-synergistic fertilizer reached 1.0:13.5, and increased income 2777.5 ¥/hm<sup>2</sup> compared with the common fertilizer (Liu et al. 2008c).

The determination results of the nutritional index of different vegetables showed difference. The application of nano-synergistic fertilizer in radish may either increase or decrease the contents of amino acids, in which the contents of cystine, proline, leucine, phenylalanine, and methionine increased by 11.1–140.0 %, while those of tyrosine, arginine, histidine, valine, and lysine decreased by 11.1–30.0 %. After applying of nano-synergistic fertilizer in eggplant, the contents of other amino acids all increased, and the increase amplitude was 11.5–42.9 %, with the exception that the content of cystine decreased by 16.7 %. The content of pepper amino acid decreased by 42.9–72.7 % after use of nano-synergistic fertilizer, while vitamin C content increased by 155.7 %, indicating that the nano carbon had a strong activation potassium function and the quality of the pepper was improved and also its storability. The amino acid content of celery treated with nano synergistic ammonium bicarbonate was shown to be 15.4–70.0 % higher than that with urea treatment. The overall increased level of amino acid suggested that the nano-synergistic fertilizer could improve the quality and nutritional

value of celery (Liu et al. 2009b). In addition, nano fertilizer also showed varying degrees of enhancing effects on the germination, growth, and yield of peanut (Liu et al. 2005a) and wheat (Liu et al. 2008d).

## 7 Nanotechnologies in detection of hazardous substance and environment protection

As we all know that there were pesticide residues, pathogenic pathogens and their toxins exist in the environment, agricultural products, and food. The detection of them is extremely important for environmental protection as well as the improvement of the quality of agricultural products and ensuring food (feed) safety. Pathogens of animals and plants detection are the basis for the controlling of many diseases, but the current detection methods involve expensive equipment, complex operation, high cost, and long detection time; thus, they cannot achieve the requirements of simple, fast, and accurate detection. The nanotechnologies can improve the accuracy and speed of detection and may solve these problems.

### 7.1 Detection of diseases

Due to the advantages of simple, rapid, non-pollution, and the results are liable to be decided, the nanotechnologies, as rapid detection and diagnosis methods, are widely used in the fields of medical science clinical examination, food safety test, and animal epidemic surveillance, such as various kinds diseases of bovine and swine, e.g., foot-and mouth disease, bovine leukemia virus, bovine akabane virus; hog cholera virus, swine pseudorabies virus, or porcine parvovirus (Wang et al. 2012a, b)

A nanotechnology of “quick test chip of double function for capture and detection of bacteria” was developed, which may perform rapid screen and detection of bacteria. In the past, the detection of bacteria in blood of patients with sepsis needs 2–5 days, whereas using the quick test chip to detect the bacteria in the blood of patients with sepsis, it can be finished in 30 min, for an increase in detection speed of about a hundred times (Nature, Communications, 2011-11-15).

Animal infectious disease not only affects the animal farming economy, but it also poses a threat to human health. Shrimp white spot virus was detected by means of dot immunogold filtration assay and the gold test strip method, in which the detection limit of the gold test strip method was 1.0  $\mu\text{g/mL}$ , and after the use of silver enhancement, the detection limit achieved 0.01  $\mu\text{g/mL}$ . The immunochromatographic strip was used for the detection of classical swine fever virus, and the results of which could be detected in 10–15 min (Lai et al. 2003), according to the test results, swine fever immunization can be reasonably guided to

establish appropriate immunization procedures rapidly. The rabbit anti-avian influenza antibodies of H5 and H9 subtype virus was purified, which were used to produce immunogold probes with the prepared colloidal gold. The modified percolation method was then used to detect avian influenza subtype viruses H5 and H9 in the tested materials safely and quickly. The examination results could be obtained in 3 min, and the respective detection sensitivities were 1.62 and 1.25  $\mu\text{g/mL}$  (Liu et al. 2005b).

At present, based on gold labelling, studies mainly focus on rapid detection on pathogenic microorganisms. The earliest immune colloidal gold technique basing on immunomagnetic separation technology was used, which was applied successfully in the detection of 01 population of comma bacillus (*Vibrio cholerae*). The oligonucleotide microarray technology with nitrocellulose membrane as the carrier and nano gold coloring, which showed high sensitivity and specificity for *E. coli*, *Salmonella*, *Shigella*, *V. cholerae*, *V. parahaemolyticus*, *proteus*, *Listeria monocytogenes*, *Bacillus cereus* List Rand, *Clostridium botulinum*, and *Campylobacter jejuni* (Hong et al. 2005). Rapid detection of *E. coli* using an integrated handheld Spreeta TM SPR sensor was conducted, and then the colloid gold antibody as the secondary antibody was introduced; it expanded the detection signal and extended the binding process of the colloid gold antibody with microorganisms, which increased the detection precision from  $10^6$  to  $10^1$  CFU/mL (Yin et al. 2005). *V. cholerae* in aquatic products by using colloid gold immunochromatography assay was investigated (Xie et al. 2005), the results illustrated that the *V. cholerae* contents in the enrichment medium was 1 CFU/mL, which can be detected by enrichment of bacteria at 12 h using a colloidal gold immunochromatography diagnostic kit. The detection of *V. cholerae* in aquatic products by the conventional method requires a long time, of which the enrichment culture time is 8–16 h, isolation and culture time is 14–20 h, and preliminary report time need more than 30 h. According to traditional isolation, culture, and identification technologies, Lester bacteria detection requires 1–2 weeks, while only 10 min is needed to obtain the test results when using the immune colloidal gold chromatography method, the sensitivity of which reaches 87.5 %.

A nanometer polymerase chain reaction (nano-PCR) assay was developed to detect the Africa swine fever virus. The amplification was efficiently enhanced with the gold nanoparticles as thermal mediator in the amplification system, and the sensitivity of the nano-PCR was more than 1000 times than that of conventional PCR with a detection limit of ten copies and had no cross-reactions with *E. coli*, porcine pseudorabies virus, porcine circovirus type II, classical swine fever virus, porcine reproductive and respiratory syndrome virus, porcine Teschovirus 8, and encephalomyocarditis virus (Cui et al. 2012).

## 7.2 Detection of mycotoxins

Mycotoxins are toxic secondary metabolites produced by fungi. The ingestion of contaminated food or feed by humans or animals will induce poisoning or disease. The application of immune technology in mycotoxin detection showed high sensitivity and strong specificity; thus, it is suitable for food and feed examinations. The colloidal gold immunochromatographic assay was used for detecting 50 ng/mL of botulinum toxin B, the result could be obtained within 10 min when the silver enhancement is used, the detection limit may reach 50 pg/mL, and there is no cross reaction with botulinum toxin A and E. A colloidal gold test strip for the rapid detection of ochratoxin A was developed, and the detection limit was shown to be much lower than that of the current limited requirements of ochratoxin in China (Lai et al. 2008). An immunogold test strip for the detection of aflatoxin B was successfully developed by Sun (Sun et al. 2006), in which the minimum detection limit was 2.5 ng/mL and the content of aflatoxin B in food could be qualitatively or semi-quantitatively detected.

Magnetic separation technology (MST) refers to the rapid isolation of targeted biological targets using superparamagnetism of magnetic nanomaterials and by the surface modification of nanoparticles and attaining specific interaction between functionalized magnetic nanoparticle surface lands and receptors (Safarik and Safarikova 2002). The application of fast detection techniques of food based on the magnetic separation technology mainly included rapid separation and enrichment of microorganisms and rapid extraction and separation and purification of nucleic acid and protein (Weng et al. 2009). There has also been an extensive application of nanotechnologies in food safety and rapid detection (Zhou 2012).

## 7.3 Detection of pesticide residues and degradation

Modern agriculture may not be operated without pesticides. Pesticides control crop diseases and insect pests and safeguard grain yield; meanwhile, they also lead to many negative effects. Pesticide residues are pressing issues affecting the environment and safety of agricultural products (Huang et al. 2014).

Pesticide residues in food are the economic and market problem and are directly related to the health of consumers. The disadvantage of the current determination method of pesticide residues in food is a lack of the sensitivity, fast, secure, and economical method. Application of nanoparticles in analysis of pesticide residues in food may overcome the disadvantages of the current a determination method, is the research focus of analytical chemistry, and obtains an amount of innovative research achievement. Combined with biology, immunology, electrochemistry, and material technology,

nanotechnologies are important tendency for analysis of pesticide residues in food (Wang et al. 2011b).

The analysis of pesticide residues is affected by a series of problems, including complex background of sample ingredients, cumbersome pretreatment process, much time consume, low concentration of tested components, limited qualitative ability of analytical instrument, and low detection sensitivity of instruments. At present, there are many determination methods to detect the agrochemicals; the main methods are chemical method, gas chromatographic method (GS), high-performance liquid chromatography (HPLC), etc. The more precise testing methods were developed in recent years, i.e., gas chromatography-mass spectrum (GC-MS) and liquid chromatography-mass spectrum (LC-MS). A novel nanotechnology used for agrochemicals detection was widely applied. They are gold nanoparticles, carbon nano tube, quantum dots (QD), magnetic nanoparticles (MNP), TiO<sub>2</sub>, SiO<sub>2</sub>, ZnO nanoparticles and nanofiber, etc. (Yun et al. 2013). Rapid detection using gold nanoparticle can efficiently solve the above problems. Nano gold immunochromatographic and nano gold filtration assay were used for the detection of residual pesticide carbaryl, and the entire detection process required only 5 min, the respective detection limits of which were 100 and 50 µg/L. A mature detection product was developed and commercialized in China, such as the carbofuran rapid test strip.

A rapid detection method for melamine in milk and eggs using Au nanoparticles as colorimetric probe has been established. The melamine can be detected after extraction and centrifugation separation with 10 % trichloroacetic acid and chloroform. The proposed method could be used to detect melamine in milk and eggs with a detection limit of 0.1 and 2.5 mg/L (S/N=3), and the recovery are 95.0–105.0 and 98.0–104.0 %, respectively (Sun et al. 2012). A new resonance Rayleigh scattering method was developed using gold nanoparticles as spectral probe and was used for the determination of melamine in milk. The detection limit was  $2.7 \times 10^{-8}$  mol/L. It was identified that this method is practical, simple, sensitive, and selective (Zeng et al. 2011). With multi-walled carbon nanotubes, solid-phase extraction cartridge is efficient for the clean-up of the sulfonamides in animal tissues or products, and the method is simple, accurate, and suitable for the quantification of the sulfonamides residues (Zhao et al. 2014).

Pesticides degradation by microbial and nanotechnologies are promising techniques which have appeared in recent years. Nano TiO<sub>2</sub> has the advantages of low toxicity, high safety, high stability, high catalytic activity, quick effect, and low energy consumption. The degradation of pesticide of chlorpyrifos in apple and damson with nanotechnologies were investigated (Wu et al. 2012). Through the treatment of nano TiO<sub>2</sub> hydrosol light or powder solution light, the degradation rates of chlorpyrifos in apple and plum were both significantly higher than the rates of degradation under natural conditions.

The degradation rate of treating 1 h is higher than the rate of 5 h (Table 6).

When nano TiO<sub>2</sub> powder or hydrogel was added in treating agent, both may more efficiently degrade the residues of chlorpyrifos in apple and plum. The photocatalytic effect of TiO<sub>2</sub> hydrogel was shown to be stronger than that of nano TiO<sub>2</sub> powder. It was confirmed that nano TiO<sub>2</sub> may effectively degrade chlorpyrifos in vegetable, with a degradation rate of reaching 70.2 % (Wang et al. 2007). TiO<sub>2</sub> can also degrade dimethoate and dichlorvos in aqueous solutions under different conditions. There have been more and more research and application of nanotechnologies in wastewater treatment of insecticide factories (Ren 2004), sewage treatment in dyeing and printing factories (Zhang and Zhu 2011), and indoor air purification (Yang 2011).

The effects of temperature on the photocatalytic degradation of 11 organophosphorus pesticides residues in the vegetable were investigated. The Chinese cabbage was treated by nanotechnology device (TiO<sub>2</sub>-ZnO compound) at different temperatures. The results showed that the degradation rate increased with the temperature decreasing from 30 °C to 0 °C. The longer the treatment time, the higher degradation rates of the pesticide residues, and the increases of the degradation rate tend to flat after 1 h treatment. The 400-W power of ultraviolet mercury lamp irradiation can increase the degradation rates of the organophosphorus pesticide residues in the vegetables (Zhang et al. 2008b).

*Application of nanotechnologies in analysis of pesticide residue* A multi-residue analytical method based on solid-phase extraction with multi-walled carbon nano-tubes as adsorbent was developed (Zhao et al. 2009). The determination of 16 organophosphorus pesticides in vegetables (including cucumber, grape, tomato, cabbage, leek, ginger, and onion) was carried out by gas chromatography-flame photometric detector (GC/FPD). Two columns (HP-50 for the analysis and HP-1 for the validation) and two flame photometric detectors were used in this method. The results indicated that multi-walled carbon nano-tubes solid-phase extraction cartridge was efficient clean-up method to vegetables (including sulfur-containing vegetables) because it reduced the contamination of the coloring background to gas chromatography-

flame photometric detector. The composite nano devices can also significantly reduce nitrate and nitrite content in Chinese cabbage, in which the decreased amplitude was positively associated with the treatment time, and the vitamin C in vegetables was not destroyed (Zhang et al. 2008b).

Nanoparticle of Fe<sub>3</sub>O<sub>4</sub>@ZrO<sub>2</sub> possesses the characteristics of selectivity enrichment of organophosphorous pesticides and superparamagnetic advantage by the external magnetic field implementation of absorption and enrichment of Fe<sub>3</sub>O<sub>4</sub>@ZrO<sub>2</sub> on organophosphorous pesticides, then performed measurement by inductively coupled plasma-atomic emission spectrometry (ICP-AES), which improved the detection sensitivity of organophosphorous pesticides, and the interference of inorganic phosphorus was very small (Wu et al. 2010). In addition, the experimental procedures were simplified and the cost of testing was reduced. Therefore, this method is suitable for the analysis and measurement of trace organic phosphorus residual on the surface of fruits and vegetables.

#### 7.4 Nanotechnologies used in environmental protection

Along with the acceleration of industrialization progress, the environment pollution is increasingly severe in China. It is the basic state policy to strengthen the environmental protection and taking effective measures to reduce pollution and protect the environment is instant. First of all, it has to strengthen the monitor and detection, and then the effective measures can be made and implemented. A new type of sensor which is made of nanomaterials possesses high sensitivity and precision; it can be used in the survey of hazardous substance in the environment and biodiversity.

Nanotechnologies can reduce greenhouse gas emissions and make the air clean (Xiang et al. 2005); it also can be used in sewage treatment (Sun et al. 2011; Ma et al. 2012), including surface water (Wilcoxon 2000) and ground water (Elliott and Zhang 2001). The removal ratio of formaldehyde in the TiO<sub>2</sub>/vacuum ultraviolet process was much higher than that in the TiO<sub>2</sub>/ultraviolet or vacuum ultraviolet photolysis process. Deposition of Au nanoparticles on TiO<sub>2</sub> significantly improved the separation of photogenerated electrons and holes.

**Table 6** Degradation of chlorpyrifos (Dursban) in fruits after treatment with different nanomaterials

Treatments	Degradation rate of chlorpyrifos in apples (%)		Degradation rate of chlorpyrifos in plums (%)	
	1 h	5 h	1 h	5 h
Natural condition illumination (control)	32.11	46.46	40.48	74.70
Nano-TiO <sub>2</sub> hydrosol illumination	46.05 (42.97 <sup>a</sup> )	60.38 (29.96)	72.64 (79.45)	80.01 (7.11)
Nano-TiO <sub>2</sub> powder solution illumination	41.18 (28.25)	53.12 (14.33)	68.46 (69.12)	76.21 (2.02)

<sup>a</sup> The numbers in the brackets represent the increased percent of degradation compare with the control

Accordingly, in the vacuum ultraviolet photocatalysis, Au/TiO<sub>2</sub> not only increased the removal ratio of formaldehyde, but also significantly decomposed the ozone. The concentration of residual O<sub>3</sub> was decreased 32 %. Moreover, Au/TiO<sub>2</sub> film was stable in the vacuum ultraviolet photocatalysis process (Li et al. 2010).

Nano-activated carbon fibers can be used in the treatment of piggery wastewater and removing nitrogen and phosphorus. The equipment is simple and the running costs are low, and the ecological benefits are obvious. The rates of removal of total nitrogen reached 59.7–75.4 %, chemical oxygen demand (COD<sub>Cr</sub>) 58.7–71.6 %. In the whole process, nano-activated carbon fibers can keep good performance in the treatment (Zhao et al. 2013). Activated carbon supported platinum catalysts (Pt/AC) can be used for the efficient removal of formaldehyde in air (Huang et al. 2013).

Magnetic nanospheres coated with polystyrene (Fe<sub>3</sub>O<sub>4</sub>@PS) which was round shape with diameter of 55±11 nm and can remove the organochlorine pesticides from aqueous solutions. The pesticides could be effectively adsorbed and the adsorption equilibrium time was less than 20 min. The sorbent of Fe<sub>3</sub>O<sub>4</sub>@PS showed a good performance with more than 93.3 % pesticides removal in treating actual water samples (Lan et al. 2014). The nanotechnologies have bright application prospect in eliminating the heavy metal pollution (Singh et al. 2011; Chrysochoou et al. 2012) and remediation contaminated soil (Gao and Zhou 2013; Satapanajaru et al. 2008; Wang et al. 2010b).

The biofilters with nano-ecobase could remove the nitrite effectively. The mean ammonia and nitrite removal rates were 93.5 and 69.3 %, respectively. The highest ammonia removal rate was 94.6 % at 30 °C, dissolved oxygen concentration of 5.43 mg/L, and hydraulic retention time of 0.33 h. The highest nitrite removal rate was 71.5 % at 21 °C, dissolved oxygen concentration of 6.40 mg/L, and hydraulic retention time of 0.33 h. The optimum operating conditions of the nano-ecobase were 30 °C, dissolved oxygen concentration of 6.40 mg/L, and hydraulic retention time of 0.33 h (Song et al. 2012).

*Application of nanotechnologies in air pollution, environmental protection, and other aspects* Nanotechnology, information technology, and biotechnology will become the three pillars of the development of social economy in the new century. Nanoparticles form the basis of nanotechnology, and functional nanomaterials are the most dynamic field of nanotechnologies, which will produce far-reaching effects and have a broad prospect of application in information, biology, energy, environment, aerospace, and other high-tech fields.

*Application of nanotechnologies in the treatment of harmful gas* Overproof contents of sulfur dioxide (SO<sub>2</sub>), carbon monoxide (CO), and nitrogen oxides in air, such as smog (PM<sub>2.5</sub>),

create harmful gases affecting human health. The application of nanotechnologies can ultimately solve the pollution source problems which produce these gases. Gasoline and diesel used in automotive fuel and industrial production include compounds containing sulfur and during combustion will produce SO<sub>2</sub> gas, which is the largest source of SO<sub>2</sub>. Nano cobalt titanate (CoTiO<sub>3</sub>) is a very strong type of oil desulfurization catalyst. Recent research results demonstrated that nano powder of composite tombarthite compounds had very strong oxidation reduction performance, the application of which may completely solve the pollution problems of carbon monoxide and NO<sub>x</sub> in automobile exhaust gases, which cannot be matched by any other automobile exhaust purification catalyst. Formaldehyde, toluene, and other gases produced by building and decoration are the main indoor pollutants. Nano TiO<sub>2</sub> had the best degradation efficiency on the above pollutants, of which the degradation rate reached nearly 100 %. The degradation mechanism is that these harmful substances are transformed into carbon dioxide, water, and organic acid under illumination conditions. The photocatalyst nano TiO<sub>2</sub> can also be used for industrial waste gas treatment of petroleum, chemicals, and other industries.

*Application of nanotechnologies in wastewater treatment* Sewage usually contains toxic and harmful substances, suspended matter, sediment, rust, odor pollutants, bacteria, and viruses. Sewage treatment is a process for the removal of the toxic and harmful substances from water. Nanotechnologies can extract and purify precious metals such as gold, ruthenium, palladium, platinum, and other metals from sewage; thus, harmful substances are transformed to useful ones. There is a new type of nanometer-purifying agent which has strong absorption capacity; its adsorption and flocculation ability is 10–20 times that of the ordinary water purification agent aluminum chloride (AlCl<sub>3</sub>). Therefore, it can completely adsorb and filter out suspended matters in sewage. The purification device, made of nano magnetic material, fiber, and activated carbon, can effectively remove rust, sediment, and odor pollutants from water. After the first two purification steps, the water is clear and has no peculiar smell and has a pleasant taste. After additional treatment with the processing device with the special water treatment membrane of nano aperture and ceramic balls with different nano aperture compositions, 100 % of bacteria and viruses may be removed, and high-quality drinking water was obtained.

The cell activity is lost and the bacteria are killed by the commonly used bactericides Ag and Cu. However, the dead bacteria may release pyrogenicity and toxic components such as endotoxin. Not only can the photocatalytic properties of nano TiO<sub>2</sub> kill bacteria in the environment, but it can also degrade toxic compound released by the dead bacteria. For example, the nano TiO<sub>2</sub> photocatalyst placed in hospital wards, operation rooms, living spaces, and other bacteria

intensive places has deodorization roles and can accelerate the degradation of city life trash. Nano TiO<sub>2</sub> surface possesses super hydrophilicity and super lipophilicity; thus, the surface of nano TiO<sub>2</sub> coating has a self-cleaning function and the characteristics of antifouling, antifog, and easy washing and drying.

## 8 Potential risks of nanotechnologies

Nanotechnology is a frontier area of science and technology which has been developing rapidly in recent years and has wide application prospects in materials, life, information, environment, energy, and national security (Bai et al. 2009). But, nanotechnology is also a double-edged sword; although nanotechnologies can be used in many areas and many beneficial effects have been achieved, it also involves many adverse effects or unclear hazards to humans, animals, plants, and the environment. Government and regulatory authorities (regulatory agencies, certification bodies) as well as environmental, health and safety councils (such as Environment Health Services), non-governmental organizations, and scientific authorities all over the world are realizing the importance of nanotechnologies risk assessment (Vyom et al. 2012), and have given their own suggestion, view, and guidance (USEPA 2007; RS/RAE 2004; COT-COM-COC 2005; Scenihr 2009; SCCP 2007; Dhawan et al. 2011; FOE 2006).

### 8.1 Effects of nanotechnologies on human health

There are four pathways by which nanoparticle may enter the human body: inhalation, swallowing, absorption from skin, and deliberate injection during medical processes (or release from implants). Due to the fact that the particle diameter of nanoparticles is extremely small, once they have entered the human body, they have a high degree of mobility. In some cases, they can even cross the blood-brain barrier.

The potential danger to human and animals of nanoparticles does not allow neglect. Researchers from Missouri University of USA found in their recent study that the residue in fruits of nanoparticles can enter into the human body. It also is possible to get in to the spleen, brain, liver, heart, etc., vitals, through blood and lymphatic system. It was demonstrated that the nanoparticle residue is very difficult to be cleared away by common methods of rinsing. Therefore, they appeal that nanotechnologies should be used with caution in food wrappages (<http://phys.org/print296407164.html>).

*Adverse effects of some nanotechnologies applications* The toxicity of nanoparticles has focused on the respiratory exposure in mammalian models and the implications for human health (Handy and Shaw 2007). With the rapid development of nanotechnologies, there is an increasing risk of human and

environmental exposure to nanotechnology-based materials and products. As water resources are particularly vulnerable to direct and indirect contamination of nanotechnologies, the potential toxicity and environmental implication of nanotechnologies to aquatic organisms must be further evaluated (Wang et al. 2008).

The suspension stability of TiO<sub>2</sub> nanoparticle in water had been investigated (Hao et al. 2009). One hundred and 200 mg/L TiO<sub>2</sub> nanoparticle caused statistically significant decrease in superoxide dismutase (SOD), catalase (CAT), and peroxidase (POD) activities and significant increase in lipid peroxidation (LPO) levels in tissues, suggesting that the fish exposed to these two concentrations of TiO<sub>2</sub> nanoparticles suffered from the oxidative stress. A comprehensive toxicity assessment, including modified acute (72 h) and chronic (21 days) toxicity tests as well as TiO<sub>2</sub> nanoparticles accumulation analysis using *Daphnia magna* as a model organism, was conducted (Zhu et al. 2010a, b). The researchers found that TiO<sub>2</sub> nanoparticle exerted minimal toxicity to daphnia within the traditional 48-h exposure time, but caused high toxicity when the exposure time was extended to 72 h. This demonstrates that the exposure duration may be a contributing factor in nanoparticle-mediated toxicity. Moreover, upon chronic exposure to TiO<sub>2</sub> nanoparticles for 21 days, daphnia displayed severe growth retardation and mortality as well as reproductive defects. The potential toxicity of two commercially used nanomaterials, namely, TiO<sub>2</sub> nanoparticle and quantum dots, using the unicellular green alga *Chlamydomonas reinhardtii* as a model system were assessed (Wang et al. 2008). The growth kinetics showed that growth inhibition occurred during the first 2 to 3 days of cultivation in the presence of TiO<sub>2</sub> nanoparticle or quantum dots. In addition, quantum dots were found to be more toxic to *Chlamydomonas* cells than TiO<sub>2</sub> nanoparticle under experimental conditions. These results indicate a potential risk from TiO<sub>2</sub> nanoparticle released into the aqueous environment.

*Nanoparticle-induced DNA damage* Genotoxicity is a central element of risk assessment of any chemical compound to which humans may be routinely exposed to (e.g., in foods or personal care products). Information regarding genotoxicity is vital as not only can DNA damage initiate cancer development, but it may also have an impact upon fertility and the health of subsequent generations if disturbances arise in reproductive cells (Singh et al. 2009). Nanoparticle has been shown to possess genotoxic potential (Karlsson 2010), which may be attributed to following main reasons.

*Direct interaction with DNA* Nanoparticles may gain direct access to DNA after being transported into the nucleus (Chen and Mikecz 2005). The entry of nanoparticles into the nucleus has been demonstrated by several studies (Alkilany and Murphy 2010; Shukla et al. 2011a). The nanoparticle is unable

to cross the nuclear membrane and thus accumulates in the cytoplasm, where they can gain access to the nucleus during mitosis when the nuclear membrane breaks down (Singh et al. 2009). The direct interaction of nanoparticle with the DNA and DNA-related protein may lead to physical damage in the genetic material. Interference with the structure or function of the DNA repair enzymes in the nucleus may be another reason for DNA damage.

**Oxidative DNA damage** Nanotechnologies, due to their high surface-area-to-volume ratio, are known to produce reactive oxidative species (ROSs). Reactive oxidative species can induce DNA damage in the forms of single- and double-stranded DNA breaks, base modifications, and DNA cross-links (Toyokuni 1998).

**Cytotoxicity of nanoparticle** Different categories of nanoparticle have been reported to cause a decrease in cell viability (Albers et al. 2011; Kang et al. 2012; Kumar et al. 2011; Mittal et al. 2011; Sharma et al. 2011; Shukla et al. 2011b). The safety/toxicity aspects of nanomaterials have lagged far behind the rate at which they are being produced. A multidisciplinary team effort consisting of material scientists, molecular biologists, toxicologists, and physicists is necessary, as it will facilitate the interlinking of different facets of nanotoxicology, thereby aiding in the understanding of cellular responses to nanomaterials exposure and the mechanisms involved. There is also a need for more comprehensive studies to fully understand and address the potential risks of engineered nanomaterials to human health and the environment. This will help in creating environment-friendly and biologically safe nanoparticle.

## 8.2 Nanotechnologies and environmental issues

Nanomaterial size, shape, specific surface area, and surface modification will all affect toxicity. In addition, environmental characteristics, such as pH value, temperature, and light density, will also affect the toxicities of nanotechnologies. The same nanomaterial, but with different diameter, length, crystal structure, and surface modification, will have different toxicities.

**Effects of nanotechnologies on the ecological toxicity** The different aqueous suspensions of nanotechnologies, such as nZnO, C<sub>60</sub>, nTiO<sub>2</sub>, single-walled carbon nanotubes, multi-walled carbon nanotubes and nAl<sub>2</sub>O<sub>3</sub>, are all able to inhibit the growth of algae (*Scenedesmus obliquus*), as well as prevent *D. magna* movements, and can lead to death. However, the toxicities of several nanomaterials are not the same as each other (Wang et al. 2008). According to the EC values of six types of nanomaterials on the growth of *S. obliquus* at 96 h, the order of the toxicities is as follows: nZnO > C<sub>60</sub>, TiO<sub>2</sub>,

multi-walled carbon nanotubes, single-walled carbon nanotubes > nAl<sub>2</sub>O<sub>3</sub>. According to the EC values on the inhibition of *D. magna* movement at 48 h, the order of the toxicities of the six types of nanomaterials aqueous suspensions are as follows: nZnO > single-walled carbon nanotubes > C<sub>60</sub>, multi-walled carbon nanotubes > nTiO<sub>2</sub> > nAl<sub>2</sub>O<sub>3</sub>. The effects of different particle sizes of Ag nanoparticle (61, 25, and 5 nm) on ryegrass growth, seedling height, and biomass were investigated (Yin et al. 2011); the nanoparticle size is smaller; and then its toxicity is stronger. Yang et al. (2010) investigated the bacteria inhibition effects of different lengths of single-walled carbon nanotubes (<1, 1–5, and 5 μm) on *Salmonella typhimurium* and found that the antibacterial ability of single-walled carbon nanotubes increased with the increase of their lengths.

## 8.3 Social risks of nanotechnologies

As a new pollutant, nanotechnologies have been given increasing amounts of attention. Researches by scholars from around the world on the ecological toxicity of nanotechnologies have mainly concentrated on the particle properties of nanomaterials and their environmental characteristics, but there has been little research performed on the relationship between the ecological characteristics of the tested species and toxicity of nanomaterials.

Nanotechnologies show broad application prospects in chemistry and chemical engineering, biomedical, composite materials, information technology, catalysts, and other aspects, due to their small size effect, surface effect, quantum size effect, and macroscopic quantum tunneling effect (Krrlik and Biffis 2001; Long and Yang 2001; Kong et al. 2000). Nanotechnologies have been widely used, but at the same time will inevitably be released into the environment, which causes adverse effects on the ecological system. The toxicities of nanoparticle and nanomaterials on the entire ecosystem have been observed, and there have been large numbers of ecotoxicological research reports on these emerging contaminants.

Among the researches on different nanotechnologies, 31 % were on the nano TiO<sub>2</sub>, followed by nano Co (18 %), nano ZnO (17 %), nano Ag (13 %), single-wall carbon nanotubes (9 %), and nano CuO (9 %) (Kahru and Dubourguier 2010). Studies on the ecological toxicity of nanotechnologies have mainly concentrated on nanomaterial properties, such as particle size, specific surface area, zeta potential, and interaction between nanotechnologies and the environment (such as light intensity, pH value) (Yang et al. 2010; Yin et al. 2011; Vecitis et al. 2010; Jin et al. 2010; Li et al. 2011b), while there has been little research on the effects of nanotechnologies on the entire ecosystem, such as on ecosystem diversity (Song et al. 2011).

**Toxicity of nanotechnologies on cells** A variety of engineered nanomaterials, with different chemical compositions and synthesized through different methods, differing in size, shape, surface coatings, etc., have been shown to be genotoxic and cytotoxic in different organ-specific cell lines (in vitro) and mice (Vyom et al. 2012). Nanomaterials may cause cell structure damage, decrease survival rate, break DNA chains, and eventually lead to cell apoptosis (Hu et al. 2010; Heinlaan et al. 2008; Kim et al. 2010; Kang et al. 2009).

**Toxicity of nanotechnologies on microorganisms** The inhibition and killing effects of nanotechnologies on a variety of pathogenic microorganisms have been discussed in the section of this paper “5. Development of new type of nanotechnologies pesticides and plant protection.” Of course, the nanotechnologies also inevitably will produce toxic side effects on some beneficial microorganisms. The toxicity of nanotechnologies on microbial is mainly exhibited in growth inhibition, inhibition of cell wall formation, or cell morphological damage, which thus exert an influence on the microbial community. Graphene and grapheme oxide may both lead to cell membrane damage ruptures of gram-negative bacteria (*E. coli*) and gram-positive bacteria (*S. aureus*), resulting in leakage of intracellular substances and thus cell death (Akhavan and Ghaderi 2010). Nano TiO<sub>2</sub> and nano ZnO also affect the soil microbial community, reduce the quantity and diversity of microorganisms in soil, and change soil microbial community compositions (Ge et al. 2011).

**Toxicity of nanotechnologies on animals** The toxicity mechanism of multi-walled carbon nanotubes on the immune system of mice was investigated, in which the immunological function of the mice was inhibited after continuous inhalation of 1 mg/m<sup>3</sup> multi-walled carbon nanotubes for 14 days (Mitchell et al. 2009). Three types of nanomaterials, nano Ag, nano ZnO, and nano TiO<sub>2</sub> could all cause oxidative damage in rat spleen and thymus and stimulate the immune system to produce an immune response (Liu et al. 2010). However, the toxicities of these three types of nanomaterials were different, which may be attributed to the particle size, shape, chemical composition, dosage, and other factors. It was found that intraperitoneal injection of 200 mg/kg nano ZnO showed mild effects on male mouse liver, kidney, and heart function, and the nano ZnO also affected the live sperm rate and led to sperm deformity (Guo et al. 2010). The dosage of 500 mg/kg nano ZnO showed significant effects on male mouse liver, kidney, and heart function and also affected the quality and quantity of mouse sperm and induced the apoptosis of spermatogenic cells. By investigating effects of carbon nanotubes on the reproductive systems of mice, Bai et al. (2010) discovered that carbon nanotubes caused reversible testicular injury without affecting the fertility of male mice. In brief, carbon nanotube treatment-induced oxidative damage

and spermatogenic epithelium thickness decrease in male mice after 15 days, which were respectively recovered through self-repair in 60 and 90 days and did not affect the fertility of male mice. The oxidative damage and stress effects of nano and conventional TiO<sub>2</sub> and ZnO suspension on the gills, digestive tract, and liver were investigated by using zebrafish (*Danio rerio*) as the tested animal (Xiong et al. 2010). The dosage of 50 mg/L nano TiO<sub>2</sub> or 5 mg/L nano ZnO suspension had serious oxidative stress effects on the digestive tract and liver of the zebrafish. Meanwhile, the same dosage of the two nanomaterials suspension caused peroxidation injury of different cell fractions of zebrafish liver cells, indicating that the toxicity of the reactive oxygen species produced by nanoparticles in zebrafish in vivo is its important toxicological effect mechanism.

**Toxicity of nanotechnologies on lower plants** There have been many studies on the toxicity of nanotechnologies on aquatic plants and algae, but little research on the toxicity of nanotechnologies on higher plants.

**Toxicity of nanotechnologies on algae** Nanotechnologies show a certain effect on the growth of algae, chlorophyll contents, protein content, and enzyme activity, and its toxic effects were involved in nanomaterial shape, size, chemical composition, concentration, solubility, and dispersibility in an aqueous solution. In addition, the toxic effects also depend on the cell structure and physiological and biochemical characteristics of the tested algae (Park et al. 2010; Zhu et al. 2008). It was found that 1 mg/L nano Ag could significantly inhibit the growth of *Microcystis aeruginosa* and the inhibitory rate was 87 % (Park et al. 2010). The *Chlamydomonas reinhardtii* was treated with silver nanoparticle modified by carbonate, and the results showed that nano silver affected the photosynthesis of *C. reinhardtii* (Navarro et al. 2008). The toxicity mainly originates from the release of Ag<sup>+</sup> by silver nanoparticle. The effects of nano TiO<sub>2</sub> on the growth dynamics and lipid peroxidation of *C. reinhardtii* showed that growth inhibition and oxidative stress appeared 2–3 days after mixed culture. Furthermore, the aggregation of cells with nanotechnologies in a medium could be seen, and the EC<sub>50</sub> of 72 h was 10 mg/L (Wang et al. 2008). The EC<sub>50</sub> values of nano ZnO, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> on the growth of *Scenedesmus obliquus* at 96 h were 1.049, 15.262, and >1000 mg/L (Zhu et al. 2008). The EC<sub>50</sub> value of nano TiO<sub>2</sub> on green algae *Pseudokirchneriella subcapitata* at 72 h was 16–26 mg/L (Warheit et al. 2007).

**Toxicity of nanotechnologies on higher plants** There were differences in the toxic effects of nanomaterials on plants, depending on the different materials and species. Oxidative stress may be one of the important methods of inhibition of plant growth by nanomaterials. Lin et al. (2009) believed that



carbon nanomaterials, including single-walled carbon nanotubes, multi-walled carbon nanotubes, and carbon, may be absorbed by rice, then transported and transferred to the next generation. Meanwhile, Begum et al. (2011) found that graphene could inhibit the growth of cabbage, tomato, and spinach, which was mainly exhibited in the fact that the root length, seedling height, leaf number, leaf area, and plant aboveground and underground biomass were decreased significantly in a dose-dependent manner. The toxicological mechanism may be that the graphene induced reactive oxygen species overproduction in plants *in vivo*, resulting in oxidative stress and plant growth inhibition. By means of nutrient solution culture experiments, the effects of nano rutile TiO<sub>2</sub> and the suspension of artificially synthesized nanomaterials of multi-walled carbon nanotubes on maize seedling biomass, root morphology, antioxidase activity, and anti-lipid peroxidation were investigated (Wang et al. 2010d). Nine days after culturing in nanomaterial suspension culture, the nano rutile TiO<sub>2</sub> was shown to have a significant inhibitory effect on the growth of the maize plants. The dry weights of roots treated with the 50, 100, and 200 mg/L concentrations were respectively 40.3, 48.1, and 62.0 % lower than those of the control, while the inhibition of the multi-walled carbon nanotubes on plant growth was not evident. The effects of nano SiO<sub>2</sub> with different particle sizes (20.3, 49.8, and 80.0 nm) and different concentrations on the seed germination and seedling growth of rice were investigated (Yang et al. 2009). By using the linear regression equation, the results demonstrated that SiO<sub>2</sub> with particle sizes of 20.3, 49.8, and 80.0 nm were significantly and positively correlated with multi-scale nano SiO<sub>2</sub> concentration ( $P < 0.01$ ). The inhibitory concentration 25 (IC<sub>25</sub>) of the inhibition rates of the three concentrations of SiO<sub>2</sub> on rice germination rate, germination state, germination index, vigor index, root length, and shoot length were respectively 8.82, 5.09, 3.62, 0.58, 1.85, and 4.96 g/L; 10.25, 8.45, 4.66, 2.34, 2.69, and 5.11 g/L; and 13.89, 7.72, 4.71, 2.97, 3.01, and 4.83 g/L. The effects on the sensitivity of each index were as follows: vigor index > root length > germination index > bud length > germination potential > germination rate. The toxicities of multi-scale nano SiO<sub>2</sub> on rice may be judged according to the inhibitory concentration (IC) of the most sensitive indicator: 20.3 nm > 49.8 nm > 80.0 nm. The critical index analysis results showed that the critical values of 20.3, 49.8, and 80.0 nm SiO<sub>2</sub> were 38.9, 257.9, and 764.1 mg/L, respectively, suggesting that the direct toxicity of SiO<sub>2</sub> nanoparticles decreased with the increase of particle size.

Extensive application of metal nanoparticles is attracting more attention because of their potential environmental risks. In the adsorption and uptake of CuO nanoparticles on the wheat root by applying different metal competing ions (Na<sup>+</sup>, Mg<sup>2+</sup>, and La<sup>3+</sup>), surfactant (i.e., sodium dodecyl benzene sulfonate, SDBS), or complexing agents like NaOAc and Na<sub>4</sub>EDTA as well as ultrasonic technique, some CuO

nanoparticles are strongly adsorbed on the plant root surface, and part of them by mechanical adhesion. Competing ions could not desorb the CuO nanoparticles from the root surface, while NaOAc and Na<sub>4</sub>EDTA well dissolved the adsorbed CuO nanoparticles. In addition, the uptake and adsorption of CuO nanoparticles increased with increasing exposure concentrations of CuO nanoparticles in the range of 5–200 mg/L. The amount of CuO nanoparticle adsorption is always lower than that of their uptake (Zhou et al. 2011).

## 9 Conclusion

In 2008, the global nanotechnologies market was \$700 billion. According to various forecasts, in 2015, the world nanotechnologies industry market size will reach \$2.6 trillion, and 7 million high skill and high wage jobs will be created, which is equivalent to the sum of the combined industries of information technology and communication. Many countries will increase investment and research and development efforts in this field to improve competitiveness. For research and development investment in nanotechnologies, the USA invested \$3.7 billion in 2005–2008, the Sixth Framework of Europe in 2002–2006 invested €1.4 billion euros, and Japan invested \$875 million in 2004. Under the support and participation of governments, various industry associations, enterprises, and private companies (research institutes), India has made great progress in the research and application of nanotechnologies and is taking the leading position among developing countries (Sarma and Anand 2012). In recent years, China has also attached great importance to the research of nanotechnologies and focused large amounts of manpower, financial resources, and material resources for research and development in this field. From central government to local authorities, from industry to departmental agencies or companies, China have set up dozens of projects of various types for funding research and application of nanotechnologies. For example, researches on nanotechnologies have been supported by the National Key Basic Research Development Plan (973-plan), National High-Tech Research and Development Program (863 plan), National Science and Technology Support Program, national public industry specific research, key projects, surface projects, and youth fund of the National Natural Science Fund project, provincial projects, city projects (funds), and special funds of colleges and universities. A new project of “Basic research on improving the effectiveness and security of agrochemicals by using nanomaterial and nanotechnology” was approved by “973-plan” in 2014 in China. The main purposes of the project are as follows: to improve the pesticide formulation and function of traditional agrochemicals and to develop a new type of efficient, security, and low-cost nano agrochemicals. In terms of the application of nanotechnologies,

especially in agriculture, China may be at the forefront of the world as above introduction, which is likely due to the more lenient and flexible system of China.

However, there is a dilemma in the selection and validation of the test methods for the characterization, dose selection, cytotoxicity, and genotoxicity assessment of engineering nanomaterials, due to the altered behavior of engineering nanomaterials as compared to chemicals. A multi-disciplinary team effort including material scientists, molecular biologists, toxicologists, and physicists is necessary as it will facilitate the interlinking of different facets of nanotoxicologies, thus aiding in the understanding of cellular responses to nanomaterial exposure and the mechanisms involved (Vyom et al. 2012).

The small size and subsequent larger surface area of nanoparticles not only endows them with some highly useful and specific properties, but it also renders them biologically more active, leading to unanticipated consequences on interaction with biological systems. Their smaller size also imparts a different biokinetic behavior and ability to reach more distal regions of the body (Oberdorster et al. 2005). Occupational exposure with nanotechnologies will increase with their growing production and use in society. On the other hand, environmental contamination caused by nanotechnology is yet another concern. In the water treated with nanotechnologies and used for crop seed treating, irrigation, and drinking and the feed (food) treated by nanotechnologies and used for feeding animals or direct eating by humans, whether or not they have short period or long terms and direct or indirect harm to crops or animals (people), the actual situation needs to be investigated and elucidated. These apprehensions have generated concern regarding the potential adverse effects of engineering nanomaterials on crops, human health, and the environmental safety.

Although myconanotechnology is still in its infancy, potential applications provide exciting waves of transformation in agriculture and fascinate microbiologists and other researchers to contribute to providing incremental solutions through green chemistry approaches for advancing food security (Kashyap et al. 2013).

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