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PERSPECTIVE

Perspectives on Plasma-Assisted Synthesis of N-Doped Nanoparticles as Nanopesticides for Pest Control in Crops

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To enhance crop efficiency and meet the growing global demands for food, a new agri-tech revolution has recently been triggering. Engineered nanomaterials have potential of lessening environmental impact and making agriculture more efficient, resilient, and sustainable. Nitrogen-doped nanoparticles (N-doped NPs) are a rising star toward development of new generation of nanopesticides for advanced green agriculture providing improved efficiency, new concepts for pest control and reduced pesticide resistance, which are key limitation of conventional pesticides. The objectives of this paper are (1) to provide perspectives of promising applications of N-doped NPs as emerging nanopesticides and (2) to review the opportunities which plasma-enabled NP technology for the scalable production of N-doped NPs based on a green and eco-friendly and sustainable approach. Main advantages of the N-doped NPs are their multifunctionality enabling to provide enhanced adhesion on leaves or insect bodies and several different modes of action to kill insects including physics, biochemical and catalytic that are expected to considerably reduce insects. Apart from insects, these nanomaterials can inactivate phytopathogenic bacteria and fungi throughout various mechanisms and therefore used for a broad spectrum of plant protection. In this review, N-doped ZnO and N-doped TiO_2 NPs will be introduced and reviewed as the first examples of these nanomaterials that have been successfully proven as nanopesticides. Following the first demonstration and the application of N-doped carbon dots (N-doped CDs) various, agricultural applications such as nanopesticides, pesticide nanocarriers, disease detection, and pest targeting will be reviewed showing their enormous potential to be translated into real applications. The plasma technology comes into play when the focus is on the manufacturing process of these nanomaterials, since, in pest control, producing high-quality nanopesticides is indispensable and challenging. Plasma-chemical NP processing is a green, simple, and rapid approach, compared to conventional methods and this review presents how this technology can be used to produce N-doped NPs in high quality, high quantity, low-cost and sustainable way with minimal waste, energy efficiency and without of the use of toxic chemicals. The implementation of this technology and introduction N-doped NPs as new powerful pesticidal agents could make significant impact in improved crop production.

1. Introduction

Along with the global economic expansion in the 21st century, the world population growth at an alarming rate has led to high demands on food and agriculture-based products. However, providing an adequately large amount of food from the agriculture sector becomes a challenging issue. Yet, there is also a threat from factors that influence adversely on crop productivity such as pests, fungi, and weeds. Among these factors, fungi are considered to be the

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leading cause of 70 % of frequent diseases.[1, 2] For instance, *magnaporthe oryzae* has been known as a fungus, which causes rice blast - the most severe fungal infection in rice around the globe.[3-7] *Botrytis cinerea* has a negative impact in many agricultural regions because it exists in a wide range of hosts and causes severe damage, both pre- and post-harvest.[8-11] *Rhizoctonia crocorum* is a significant cause of the rot of various parts of vegetables such as leaf spot and stem rot.[12-14] The statistical results have indicated that multiple pathogens are one of the significant causes of crop losses, and this can be seen in a variety of plants such as rice, barley, wheat, grapevine, cotton, and groundnut.[12] Therefore, controlling pathogenic microbes, which cause phytopathogen, is a significant task for not only governmental bodies but also agricultural farmers and scientists to enhance crop productivity.

Over the last century, many chemically synthesized pesticides, such as insecticides, acaricides, rodenticides, nematicides, molluscicides, and fungicides have been developed and used to improve agricultural crop efficiency as well as protecting plants from unexpected damages, such as weeds, harmful insects, pathogenic bacteria and fungi. The pesticides made an enormous contribution to improving global food production, especially in developing countries with a significant impact on the productivity of cultural heritage. However, there is still a need for improvement in the use of pesticides in agriculture as it is estimated that 20 – 40 % of global agricultural crop loss is due to pathogens, animals, and weeds. [15-17] There are several challenging problems in conventional pesticides that needs urgent solutions such as low efficiency. It is reported that 99% of utilized traditional pesticides are leaked into the groundwaters contributing to the widespread eutrophication. Their high toxicity on human and environment with many disastrous examples can be seen in the past, which leads to "pesticide resistance" of pests that current pesticides could not deal with.[18] This issue has significantly increased production cost, and heavily scrutinized the use of pesticides due to their environmental pollution, as well as posing a risk to human well-being.

These problems with conventional pesticide formulations have motivated a new research direction in the nanotechnology application. In other words, new generations of advanced pesticides have demonstrated new solutions, which are more efficient and less toxic. Accordingly, nanotechnology has become an important driver for the impending agri-tech revolution.[19] In spite of only being concerned in several decades ago, nanoscale-based science and technology have been paid more and more attention to providing innovative solutions to society, industrial and agricultural sectors.[20] The advanced applications of nanotechnology can sustainably contribute to the enhancement of crop efficiency. It is in virtue of the fact that they can protect not only plants against the impacts of phytopathogens but also monitor the development process of plants as well as guarantee the mass production of global food production.[19, 21, 22] They also enhance food quality and reduce the cost of food production as well as limiting contaminants leaked into the surrounding environment.[23-28]

Although there are still fewer studies on nanotechnology applications for agriculture compared to biomedical sectors, researchers, nowadays have paid more attention to the field because of tremendous benefits from this technology. Current nanoparticles (NPs) that have been used as nanopesticides in agriculture are silica NPs,[29-31] sulfur NPs,[32-34] silver NPs,[35-38] copper and copper oxide NPs,[39-41] zinc oxide NPs,[42-44] titanium dioxide NPs, [45-47] reduced graphene nanosheets,[48, 49] and chitosan NPs.[50-52] All of these NPs have been proven to be capable of protecting cultural heritage from disease, fungi, weed, and bacteria. The mechanism of antifungal, antimicrobial, and antibacterial activity of these materials varies based on their intrinsic properties and structure. These mechanisms include reactive oxygen species (ROS) generation under the UV and visible light irradiation, release of ions into cells, internalization of NPs into cells, and direct contact with cell membrane via electrostatic force. Among these mechanisms, ROS generation is considered to be one of the main and most effective approaches to cause damage to pathogens.[53, 54] In materials science and engineering application, some of the typical nanomaterials such as TiO_2[55] and ZnO[56] are capable of yielding ROS throughout photocatalysis. These ROS groups can decompose complex chemical compounds and inactivate a wide range of biological microorganisms.[57] However, most of these materials only exhibit strong pesticidal properties under UV exposure because of their broad energy gap, which limits their potential applications in pest control.

To overcome these drawbacks, scientists have recently focused on shifting the adsorption regions of these photo-catalysts from UV light to the visible light areas in order to enhance their intrinsic optical properties. One of the most effective and practical approaches is to dope heteroatoms on the surface of these materials.[58,59] Among heteroatoms, nitrogen doping into the surface of photocatalysts has been determined to be the most effective to narrowing the energy

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gap. As a consequence, nitrogen doping results in the shift to a stronger absorption in the visible light region.[60] In addition, some scientific research has shown that nitrogen doping into photocatalytic nanoparticles not only enhance their optical properties but also increase antifungal and antimicrobial activity in agriculture because of more ROS generation.[61] However, these nitrogen-doped materials are not yet widely used to reduce damage from fungi, weeds, and plant pathogens. Therefore, in this paper, we will review the overall applications of these nitrogen-doped nanoparticles as nanopesticides until now.

There are many methods **to** fabricate nitrogen-doped nanoparticles, including microwave synthesis,[62-64] arc-discharge,[65-67] laser ablation,[68, 69] electrochemical oxidation,[70] chemical oxidation,[71] ultrasonic synthesis,[72] hydrothermal treatment,[73, 74] thermal decomposition,[75] and plasma treatment.[76-78] Compared to other conventional synthesis methods, plasma-assisted synthesis of nitrogen-doped nanoparticles offers some promises: (1) fast, friendly-environmentally synthesis of high-quality and small-sized nanoparticles; (2) reduced starting materials and eliminated multiple steps of fabrication; (3) non-thermal controls over surface modification under atmospheric pressure with safety considerations. Additionally, antimicrobial and antibacterial properties of nanoparticles are dependent on their size and shape.[79, 80] Therefore, using plasma-assisted synthesis system can generate high quality and size-controlled nanoparticles, which can be applied widely to agriculture.

For these reasons, plasma-induced synthesis is a promising method to produce potential N-doped NPs to improve crop productivity. In this review, we will introduce an overview of nanoparticles used as antibacterial and antifungal agents in pest control in section 2. Then, we will review N-doped NPs and their agricultural applications in section 3. Later on, we will give a new perspective to make N-doped NPs using plasma-induced synthesis methods in section 4. Next, plasma-induced production of N-doped of NPs will be demonstrated as a part of a new agri-tech revolution in section 5. In section 6, we will conclude the key points of plasma-assisted synthesis of N-doped NPs for pesticidal applications in crops. Finally, we will sum up the pros and cons of plasma-assisted fabrication of N-doped NPs in pest control, and will discuss their future direction with a brief outlook in section 7.

2. The use of nanoparticles as nanopesticides

Various nanoparticle formulations have been demonstrated to be able to kill bacteria, fungi, weeds as well as fighting against plant pathogens in cultural heritage.[81, 82] Based on the purpose of agricultural applications, nanopesticides are classified into various types, consisting of nanoherbicides,[83, 84] nanofungicides,[85, 86] nanoinsecticides.[83, 84] The focus in this review is on nanopesticides, which can be synthesized and modified by plasma-assisted fabrication.

2.1. Titanium dioxide (TiO_2) NPs as nanopesticides

These nanoparticles are well known as one of the most semiconductor catalysts in the light of its physicochemical stability, cost-effectiveness, and high photocatalytic efficiency. TiO_2 NPs are non-toxic to humans, and consequently have been investigated and licensed by the American Food and Drug Administration (FDA) for launching into the commercial market.[87] Also, extensive research on TiO_2 NPs has been carried out for different organism disinfections such as viruses, bacteria, fungi, and algae. It is assumed that the antifungal and antibacterial activity of TiO_2 NPs is majorly owing to the ROS generation such as hydroxyl radicals ($^{\bullet}OH$), superoxide anions ($O^{\bullet}{}_2^-$), and hydrogen peroxide (H_2O_2) molecules.[88] In contact with microorganisms, these reactive redox species can damage their cell membrane. As a result, these microorganisms will be inactivated. The mechanism of TiO_2 generating reactive oxygen species under UV irradiation is described in Figure 1.[89]

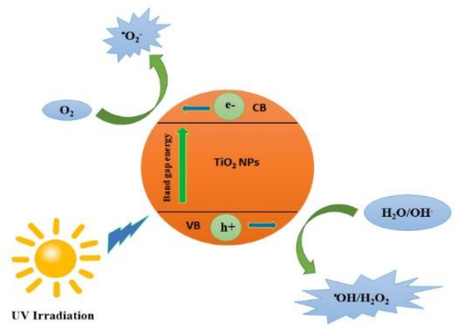

Figure 1 Mechanism of ROS generation of TiO2 NPs under UV Irradiation (This Figure is adapted with from 89 with permission of Springer Nature, 2015)

There are various pesticidal mechanisms of TiO_2 on different microorganisms, but the primary mechanism is explained due to the ROS generation under UV irradiation (Figure 2)[90]. Anatase nanoparticles are capable of inactivating *Rhipicephalus (Boophilus) microplus* larvae as well as adults of *Haemaphysalis bispinosa*.[91] The insecticidal activity of TiO_2 increased with the nanoparticle concentration in the interval of 4-20 mg.l^{-1}.[91] It is reported that after

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50 days of treatment, TiO_2 NPs can reduce a large amount of (*Hypocrea lixii*) white-rot and (*Nucor circibelloides*) brown-rot fungi, which can be observed on various types of wood such as scot pine, silver fir, walnut, wild cherry, sessile oak, beech, and ash.[92, 93] A scientific report about the pesticidal activity of TiO_2 NPs has been concluded that TiO_2 sprayed at a low concentration can reduce the severity of foliar and pod diseases of cowpea.[94] Also, it has been reported that TiO_2 NPs could improve remarkably the growth of mung bean plant. The enhancement can be seen in different parts of the mung bean plant such as shoot length (17.02%), root length (49.6%), root area (43%), root nodule (67.5%), chlorophyll content (46.4%) and total soluble leaf protein (94%), when applied.[95, 96] In another study, the enzyme alpha amylase was utilized as a reducing and capping substance for synthesis of TiO_2 NPs. These nanomaterials can also suppress the activation of *Staphylococcus aureus* and *Escherichia coli* with the minimum inhibitory concentration (MIC) value of 62.50 $\mu g.ml^{-1}$ for both bacteria strains.[97] While another research indicates that TiO_2 inhibits the growth of various types of bacteria from *Aeromonas hydrophila* to *Escherichia coli, Staphylococcus aureus, Proteus mirabilis,* and *Pseudomonas aeruginosa*.[98] To improve their efficiency, TiO_2 NPs are used in combination with other nanoparticles to inhibit harmful fungi and bacteria. Specifically, silver doped hollow TiO_2 nanoparticles with a concentration within a range of 0.02-0.52 mg/plate are effective against *Fusarium solani* and *Venturia inaequalis* in the presence of light TiO_2.[46] The pesticidal properties of TiO_2 NPs are described in Table 1.

Table 1. TiO_2 nanopesticides with antimicrobial performance against various types of microorganisms

Types	Microorganisms	Features	Ref.
Fungicides	*Candida albicans*	The concentration of TiO_2 NPs to inactivate *Candida albicans* fungi is 5.35 $\mu g.ml^{-1}$	99
Fungicides	*Fusarium solani* and *Venturia inaequalis*	The antifungal activities of Ag-doped TiO_2 NPs are enhanced under visible light exposure.	46
Bactericides & Fungicides	*Bacillus, Klebsiella, Pseudomonas, Salmonella, Streptococcus, Aspergillus niger* and *Trichoderma reesei.*	TiO_2 NPs exhibit excellent antimicrobial activity against both bacterial species and fungi.	100
Bactericides	*Pseudomonas stutzeri*	*Pseudomonas stutzeri* is inactivated during irradiation with near-ultraviolet light.	101
Bactericides	*Pseudomonas aeruginosa*	TiO_2 thin films can suppress *Pseudomonas aeruginosa* under longwave UV irradiation by ultrastructural damage on bacteria cells.	92, 102, 103
Bactericides	*Staphylococcus aureus*	*Staphylococcus aureus* can survive under low irradiation of UVA but cannot resist when exposing to TiO_2 photocatalytic coatings.	104
Bactericides	*Aeromonas hydrophila, Proteus mirabilis, Escherichia coli, Staphylococcus aureus* and *Pseudomonas aeruginosa*	TiO_2 NPs strongly inhibits the growth of these bacteria.	98
Acaricide	*Rhipicephalus microplus* and *Haemaphysalis bispinosa.*	TiO_2 NPs is demonstrated to be a highly stable nanomaterial, and remarkably inactivate the larvae of *Rhipicephalus microplus* and *Haemaphysalis bispinosa.*	91

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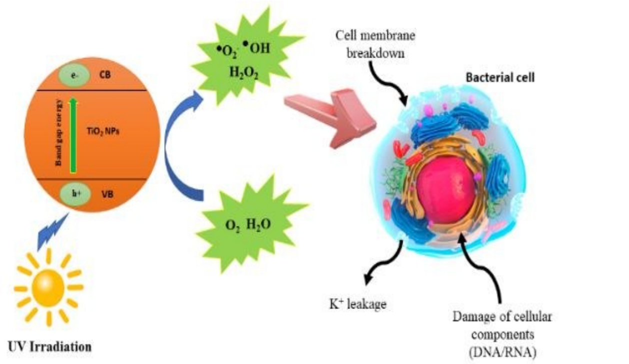

Figure 2 Antimicrobial mechanism of TiO2 nanotube under UV irradiation via ROS generation (This figure is adapted from Ref. 90 with permission from the Elsevier, 2015)

2.2. **Zinc oxide (ZnO) NPs as nanopesticides**

ZnO has been extensively used for various applications in the industry because they own typical properties such as optical properties,[105] chemical sensing,[106, 107] semiconductivity,[107, 108] electric conductivity,[109, 110] etc. Also, a direct wide energy gap of ZnO NPs (3.3 eV) can be observed in the near-UV spectrum.[111, 112]

Similar to TiO_2 NPs, research on antibacterial and antifungal properties of ZnO NP has taken a great interest from scientific communities. ZnO NPs possess attractive antibacterial activity since the surface reactivity can be improved when increasing their specific surface area. ZnO NPs have been known as photocatalytic agents that have significant impacts on chemical compounds and biological systems. Due to possessing high absorption under UV irradiation, ZnO NPs are often used in cosmetics in order to protect skin from UV light.[113] As discussed in section 2.1, ROS groups are highly stable and able to oxidize; thus, they can suppress the growth of bacteria.[114, 115]

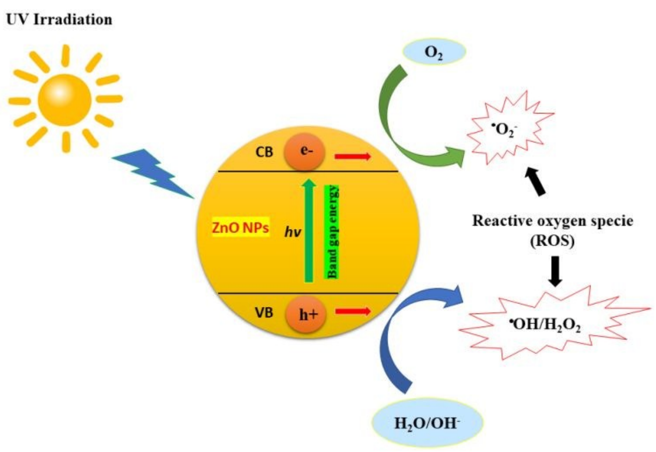

Figure 4 Proposed mechanism of photo-triggered production of ROS by ZnO NPs (This figure is Reproduced from Ref. 116 with permission from the Royal Society of Chemistry 2018)

The primary antibacterial mechanism of ZnO NPs has been concluded due to ROS generation in various studies. It is also reported that ZnO antibacterial activity could be enhanced significantly because of the large number of generated ROS when exposed to UV light. ROS such as hydroxyl radicals (•OH), superoxide anions ($O^{\bullet}{}_2^-$), and hydrogen peroxide (H_2O_2) ultimately lead to cell death. One possible explanation is that these reactive groups are engaged in the decomposition of biological components in bacteria cells such as lipids, DNA, and proteins. The ROS generation of ZnO NPs is explained in Figure 3.[116]

In particular, after releasing from ZnO NPs under UV irradiation, elevated ROS accumulates on the cellular surface of bacteria. This induces oxidative stress in cells, leading to the decomposition of cellular components. Recently, a large number of studies reveal that the ROS of ZnO NPs also cause various processes such as lipid peroxidation, enzyme deactivation, and membrane destruction.

In addition to the ROS mechanism, there are other possible antibacterial mechanisms of ZnO as shown in Figure 4,[117] including Zn^{2+} release, diffusion of ZnO into the bacteria, and subsequent electrostatic interactions.

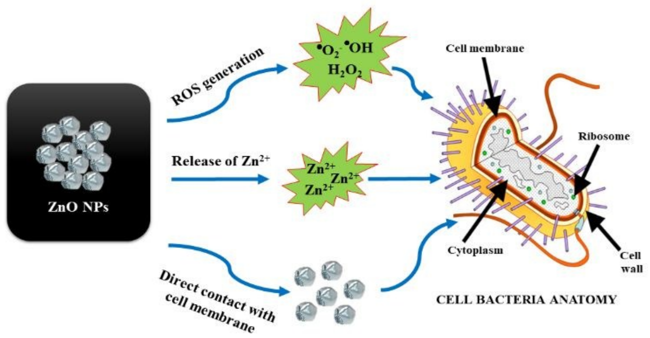

Figure 3 Various antimicrobial mechanisms of ZnO NPs (This figure is Reproduced from Ref. 117 with permission from the Royal Society of Chemistry 2019)

ZnO NPs have been widely utilized in various applications, one of which is to control plant pathogens and other pathogenic microbial entities. It has been know that fruits are one of the major agricultural products for human, and most of the plant diseases in fruit is caused by fungi.[118, 119] Many severe phytopathogens are caused by various microbial organisms like *fungus-like B. cinerea* and *P. Expansum*, and these plant pathogens can be grey and blue mold on table grapes and

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rotting of stored apples and pears.[118, 119] The ZnO NPs have inhibitory effects on the growth of *Mucor plumbeus, Rhizopus stolonifer, F. oxysporum, and A. alternata*. Additionally, *Botrytis cinerea* and *Penicillium expansum* are inactivated when exposed to more than three mmol.l^{-1} of ZnO NPs.[120] ZnO also shows intense antifungal activity against plant pathogenic fungi such as *Fusarium oxysporum, Alternaria alternata, Mucor plumbeus,* and *Rhizopus stolonifer*.[121] Pesticide properties of ZnO NPs are depicted in Table 2.

Table 2. Antifungal and antibacterial properties of ZnO NPs on plant disease

Types	Microorganisms	Features	Ref.
Fungicides	*Botrytis cinerea* and *Penicillium expansum*	The development of *Botrytis cinerea* and *Penicillium expansum* can be inhibited at a concentration of more than three mmol.l^{-1} of ZnO NPs.	122
Fungicides	*Aspergillus fumigatus* and *Candida Albicans* Yeast	ZnO have considerable antifungal activity	123
Fungicides	*Aspergillus niger*	ZnO nanopowders had biocidal activity against the fungus *Aspergillus niger*	124
Fungicides	*Fusarium oxysporum, Alternaria alternata, Mucor plumbeus,* and *Rhizopus stolonifera*	ZnO shows vigorous antifungal activity against plant pathogenic fungi	121
Fungicides	*Trichophyton mentagrophyte, Microsporum canis, Candida albicans* and *Aspergillus fumigatus*	ZnO exhibited an inhibitory effect on the growth of dermatophyte isolates.	120
Fungicides	*Fusarium graminearum*	The ZnO NPs possessed stronger inhibitory effects on fungal development than that of micro-sized ZnO particles.	125
Bactericides	*Listeria monocytogenes, Salmonella enteritidis* and *Escherichia coli*	ZnO powder shows significant antimicrobial activities against all three pathogens in growth media	126
Bactericides	*Escherichia coli*	*Escherichia coli* can survive in ZnO nanofluids. The antibacterial properties of ZnO nanofluids are based on their concentrations and particle size.	127
Bactericides	*Pseudomonas aeruginosa, Pseudomonas fluorescens, Salmonella enteritidis, Salmonella typhimurium, Staphylococcus aureus, Bacillus cereus Escherichia coli,* and *Enterobacter cloacae*	Nanoscale particles of ZnO have stronger antibacterial properties than that of conventional powder.	128

3. N-doped nanoparticles as nanopesticides

Agricultural applications of nanoparticles as nanopesticides have been comprehensively reviewed in section 2.1. It has been considered that photo-catalysis is involved in the antibacterial and antifungal activity of the materials above. However, their photocatalytic capacity is limited only under UV irradiation. It is also estimated that merely 10% of the solar spectrum can be used.[129] For this reason, it is of utmost importance to innovate novel nanomaterials that can express high photocatalytic under visible light exposure.

When the light adsorption is adjusted to visible light region, the applications of these photocatalytic nanoparticles can be extended. The most effective and practical methodology is to engineer their surface by doping with heteroatoms.[130, 131] Besides, it has been demonstrated that modifying the surface of nanoparticles by nitrogen doping could improve photocatalytic properties, which leads to the enhancement of antifungal and antibacterial characteristic, compared to original nanoparticles.[132, 133] Although there are only a few studies of nitrogen-doped nanoparticles on pest control, their applications are expected to be promising for green agriculture. Therefore, we will summarize their current use in controlling phytopathogens, and prove the impact of nitrogen doping on pesticide activity.

3.1. N-doped TiO_2 NPs as nanopesticides

As summarized in the previous sections, TiO_2 NPs have been extensively used in suppressing the growth of fungi, weed, bacteria, and other plant pathogens owing to their excellent photocatalytic property, which generates various reactive oxygen species (ROS).

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Also, by doping with nitrogen, this property has been improved significantly to kill some bacteria and fungi.

For example, nitrogen-doped metal oxide nanocatalysts such as TiO_2 achieved remarkable improvements in *E. coli* bacteria photodegradation efficiency.[134] In particular, an experiment is conducted about interactions of TiO_2 and N-doped TiO_2 nanoparticles with *E. coli* bacteria in the dark. As a result, there is no detectable suppression of bacteria overall photocatalytic nanoparticles. Otherwise, N-doped TiO_2 shows a remarkable increase in inactivating *E. coli* bacteria after 120 min of using the solar light irradiation. Another experiment is carried out to compare different nitrogen sources in improving *E. coli* bacteria suppression. The results reveal that N-doped TiO_2 nanoparticles using ethylenediamine as a precursor expressed the best performance on inhibiting the growth of *E. coli* within 90 min.

Meanwhile, N-doped TiO_2 NPs derived from ethanolamine depicted a moderate improvement in *E. coli* inhibition. It is explained that it is attributed to the Ti-N bonds existing in N-doped TiO_2 NPs. Further, it is believed that the Ti-N bond mediates the electron coupling between the titanium of TiO_2 NPs and nitrogen in the doping, thus leading to a change of the electron structure at the valence band edge. As a consequence, the energy gap of TiO_2 is narrowed.[135, 136] Especially, another evidence has been pointed out to explain the photocatalytic inactivation mechanism of *E. coli* using N-doped TiO_2.[137] Particularly, the inactivation process undergoes three stages. At the first stage, there is a relatively slower initial photo-degradation rate during the first 20 min because of the defense of *E. coli* to the ROS penetration into cell membrane. Next, more ROS is generated to overcome the defense of bacteria; consequently, the number of *E. coli* bacteria decreases rapidly. Lastly, the inactivation becomes intoxicated due to the formation of by-products, such as acids or aldehydes**.** Similarly, recent research concluded that N-doped nitrogen exhibited antimicrobial activity against *E. coli*, and the ROS generation during 15 min of visible light irradiation.[138]

The fungicidal property of the photocatalytic N-doped TiO_2 has also been researched under visible light exposure.[61] In this research, it is demonstrated that nitrogen is successfully introduced into TiO_2, and the antifungal property exhibits actively due to stronger adsorption under visible light. Typically, the synthesized N-doped TiO_2 can completely suppress the development of *Helminthosporium maydis* fungi, while they can survive in the pure TiO_2 NPs in the same condition. Biologically, *Helminthosporium maydis* is defined as a type of fungi that can cause plant pathogens via the infection of the leaf, ear, and grain. It is reported that when their spores commenced the germination in the first period, N-doped TiO_2 NPs can adhere to the cell membrane of *Helminthosporium maydis* with a negative charge. After inactivating the spores, the nanoparticles no longer adhered to the outer part of the cell membrane of *Helminthosporium maydis.*

Another study on the application of N-doped TiO_2 NPs has been conducted for inhibiting *Fusarium graminearum* – an agricultural pathogenic fungus.[139] *Fusarium graminearum* has been classified as a cause of pathogen on wheat, which could induce a considerable decrease in crop yield of grain. Additionally, it also generates various mycotoxins, which can cause disease and death in both humans and other animals. In a study, photocatalytic nitrogen-doped titanium oxide NPs modified with palladium is synthesized, which can be activated under visible light. It is demonstrated that modifying N-doped TiO_2 NPs with palladium oxide (TiON/PdO nanoparticles) could considerably enhance their photocatalytic disinfection on *Fusarium graminearum*. It is investigated that these novel nanoparticles are capable of adhering onto the surface of macroconidium. This feature might facilitate the photocatalytic decomposition of these macroconidia, as shown in Figure 5. It is also proposed that the photocatalytic antifungal mechanism of TiON/PdO nanoparticles on *Fusarium graminearum* fungi could be explained due to the invasion of generated ROS groups into their cell membrane, leading to disinfection of cellular components.

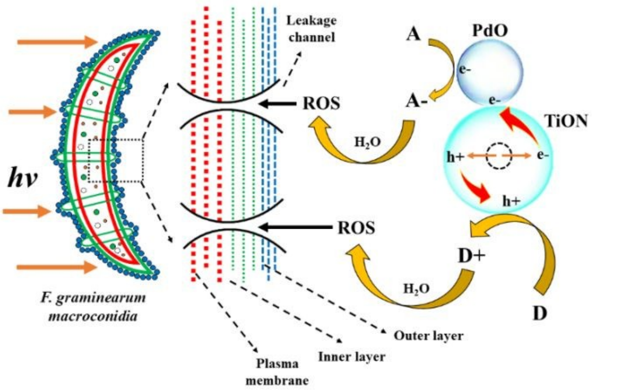

Figure 5 Antifungal mechanism of TiON/PdO NPs on Fusarium graminearum (Reproduced from Ref. 139 with permission from the American Chemical Society 2013)

3.2. N-doped ZnO NPs as nanopesticides

Until now, only N-doped TiO_2 NPs have been applied to agricultural pathogenic control. In addition, some other N-doped nanoparticles such as nitrogen-doped ZnO and nitrogen-doped carbon dots, which

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possess similar photocatalytic disinfection on plant pathogens are not widely used. This indicates a potential application of nitrogen-doped nanoparticles into pest control due to their excellent antibacterial and antifungal properties via photocatalysis.

Similar to the N-doped TiO_2 NPs, this type of nitrogen-doped ZnO nanoparticles typically exhibits stronger photocatalytic properties compared to the original ZnO.[140, 141] In addition, it is demonstrated that doping nitrogen into ZnO NPs induces a shift of the light adsorption from UV to visible light, and finally, more ROS is generated. It is because the bandgap energy is narrowed as shown in Figure 6.[140-143] Apart from that, ROS generation proves to be the primary cause of inhibiting the growth of fungi and bacteria.[144] It can be concluded that utilizing N-doped TiO_2 NPs as a photocatalyst under visible light will pave a promising way for research on pest control.

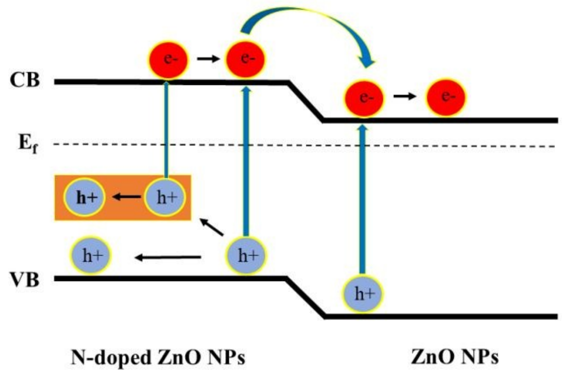

Figure 6 Comparison of energy levels and charge transfer between ZnO and N-doped ZnO NPs (Reproduced from Ref. 141 with permission from the American Chemical Society 2013)

3.3. N-doped carbon dots (N-doped CDs) as potential multifunctional nanopesticides

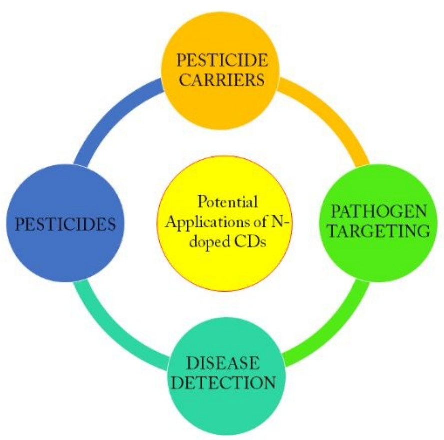

Figure 7 Various possible applications of N-CDs in agriculture

N-doped carbon dots or N-doped CDs are functionalized materials that derive from carbon dots (CDs).[145-147] Due to nitrogen doping along with available functional groups on the surface, N-doped CDs have been investigated to enhance remarkably their optical properties compared to CDs. Based on the unique features of N-CDs, potential applications of N-CDs are summarized in Figure 7.

3.3.1. N-doped CDs as potential nanopesticides

Carbon quantum dots (CQDs), also called carbon dots (CDs or C-dots) or carbon nanodots (CNDs), have been classified as one of the newest members in carbon-based materials.[148, 149] CDs are defined as discrete and quasi-spherical carbon NPs with ultrasmall particle size ranging from 1-10 nm.[150-152] Their unique properties are the integration of typical fluorescent properties of quantum dots and excellent electronic properties of carbon nanomaterials.[153] As a result, this type of carbon nanomaterial becomes more dominant than conventional semiconductors in terms of fluorescent properties and particle size. In addition, CDs are more beneficial than other traditional materials in terms of cost-efficiency, non-toxicity, photoelectric nature, and capacity for generating −/h+ pairs under UV light exposure.[154] CDs-based photocatalysts are water dissolvable and non-toxic to the human body, while the majority of photocatalysts containing metals such as ZnO and TiO_2 NPs might result in a risk of water pollution after contaminants are degraded.[155] Additionally, C-dots also exhibit the high intensity of fluorescent properties in the infrared and visible regions, as well as photochemical stability.[149] Like other conventional semiconductors (ZnO, TiO_2), CDs possess a typical energy gap between the valence and the conduction bands.[156] For this reason, they can cause photocatalytic redox reactions. It has been reported that photocatalytic properties of CDs are size-dependent.[155] In addition, CDs as a photocatalyst can generate ROSs such as superoxide shown in Figure 8, and these groups can cause the decomposition of organic compounds and the death of hypoxic tumor cells.[157] Therefore, ROS generation of photocatalytic CDs under UV light can exhibit antibacterial and antifungal activity in controlling agricultural pathogens. It is also demonstrated that CDs could inhibit the activation of E. Coli bacteria under ambient conditions.[158, 159] Thus, this means that CDs exhibit significant bactericidal functions. Vitamin C is also used as a carbon source to fabricate degradable CDs with strong antibacterial and antifungal properties using one-step electrochemical methodology.[160] These results reveal that CDs

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efficiently suppress the activation of bacteria like *Staphylococcus aureus, Bacillus subtilis, Escherichia coli, the ampicillin-resistant Escherichia coli, Rhizoctonia Solani* as well as *Pyricularia Grisea*. Various experiments have been carried out to prove the antibacterial and antifungal mechanism of CDs.[160] In particular, it is suggested that CDs could penetrate bacteria's cell membrane via diffusion process. Next, these CDs can generate ROS groups to attack the bacteria's cellular wall, and attach to the DNA and RNA of bacteria. This might have negative impacts on their genetic process, leading the death of bacteria and fungi at a very low concentration.

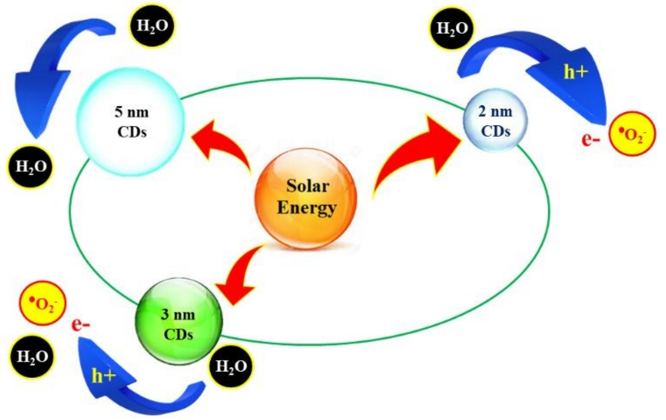

Figure 8 Mechanism of size-dependent ROS generation from CDs (This figure is adapted from Ref. 155 with permission from the Elsevier, 2019)

Although CDs can express the antifungal and bactericidal activity, these properties are not strong enough under visible light, which limits their potential applications in pest control. Therefore, nanotechnologists think of a novel solution to enhance this characteristic under visible light. One of the most efficient methods is to modify the surface of CDs by doping with nitrogen atoms to form nitrogen-doped CDs since the nitrogen atoms in CDs can provide access electrons and inject into carbon dots, thus changing their photocatalytic and optical properties.[161] As a result, the light absorption of N-doped CDs can extend from UV to visible light. Therefore, N-doped CDs are more dominant than CDs in antibacterial and antifungal activity under visible light. It is showed that 25 and 75 µl.ml^{-1} of N-doped CDs could induce 100% antibacterial activity in the case of E. Coli and S. Aureus, respectively.[146] It is concluded that nitrogen-containing groups such as amides and amines are of utmost importance to improve the antibacterial activity.[162] It is also believed that the causes of bacteria death are involved in electrostatic force between protonated forms in nitrogen-containing groups and lipids in the cellular membrane of bacteria. Another explanation for bacterial and fungal death is that CDs can produce active oxygen species to damage the cellular components of bacteria and fungi. Though there are a few studies of N-doped CDs, the evidence above strongly shows that this type of material could be a very promising candidate in inhibiting the growth of fungi- and bacteria-caused pathogens throughout photocatalysis under visible light in crops. The photocatalytic applications of N-doped CDs for bacterial and fungal inactivation is described in Figure 9.

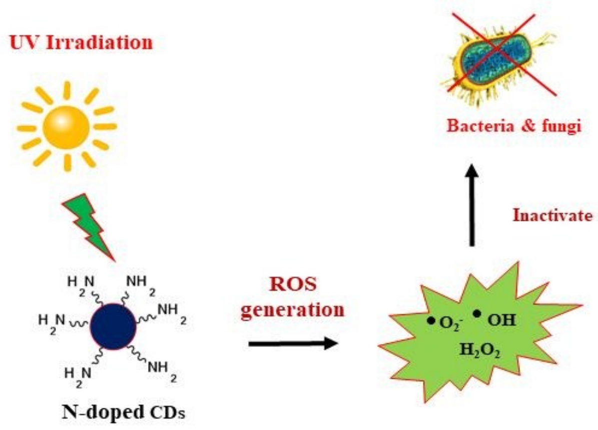

Figure 9 Proposed application of N-doped CDs as a photocatalyst for antibacterial and antifungal activity to inactivate phytopathogenic microorganisms

3.3.2. N-doped CDs as a biosensor for detecting agricultural pathogenic diseases

Apart from photocatalysis, N-doped CDs also exhibit powerful fluorescent properties, which make it distinctive from other current nanomaterials.[163] It is believed that many nanomaterials with optical properties have been used as biosensors for detecting plant pathogens.[164] For example, quantum dots (QDs) have been extensively utilized to detect plant pathogens based on fluorescence resonance energy transfer (FRET) mechanism.[165-168] The FRET mechanism relies on energy transfer between two light-reactive molecules. Some types of sensors based on QDs and FRET (QD-FRET based sensors) have been designed to detect the witches' broom disease of lime.[169] The designed QD-FRET based sensor system exhibits a very high sensitivity to this kind of pathogens in lime. Apart from that, QD-FRET based sensors are also investigated for the detection of pathogen vectors. In particular, they can detect the *beet necrotic yellow vein virus* (BNYVV) and *Polymyxa betae Keskin*. This vector is determined to be a significant cause of *Rhizomania* in sugar beet.[170] It has been demonstrated that N-doped CDs have been proved to have stronger and more stable fluorescent properties than QDs.[171] Therefore, N-doped CDs can be an alternative nanomaterial

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as biosensors to detect harmful pathogenic fungi and bacteria in crops. The proposed application of N-doped CDs as biosensors for phytopathogenic detection is described in Figure 10. Specifically, N-doped CDs is conjugated with targeting molecules such as antibiotic compounds, which can be recognized by specific cellular receptors. N-doped CDs can enter into phytopathogenic microbial cells throughout various cellular internalization. After internalization stage, these N-doped CDs in microbial cells can excite specific high fluorescence under irradiation.

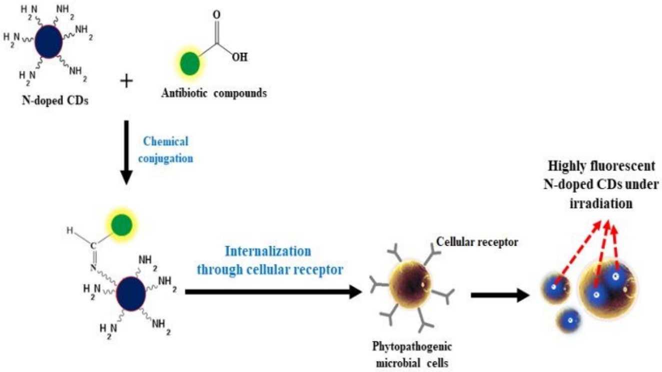

Figure 10 Proposed application of N-doped CDs as biosensors for phytopathogenic detection

3.3.3. N-doped CDs as a delivery carrier of pesticides

In addition to detecting phytopathogenic diseases based on strong fluorescent properties, N-doped CDs can also be applied for smartly targeted nanopesticides like other nanoparticles. In this case, N-doped CDs are used as a nanocarrier for delivering pesticides with controlled release instead of being used as nanopesticides themselves. In fact, nanoparticles have been widely used to deliver drugs in biomedical applications such as metal oxide NPs,[172, 173] polymeric nanoparticles,[174] mesoporous NPs,[175] but comparatively few studies have focused on agricultural applications of nanoparticles, especially N-doped CDs for controlled release of pesticide compounds to target agricultural pathogens. Like other nanoparticles, the surface of N-doped CDs can be modified to conjugate with pesticide molecules for controlled release in crops. It is believed that most of the functional groups on the surface of N-doped CDs are $-NH_2$, -OH and –COOH.[176-180] Therefore, to enhance the loading efficiency of pesticides on N-doped CDs, these nanocarriers should undergo carbodiimide crosslinking reaction with pesticides reagents. This type of reaction is one of the most popular and effective methods to carry drugs or pesticides.[181-184] In principle, carbodiimide reaction is a crosslinking reaction that carboxyl-reactive chemical groups or carboxylic acids (-COOH) react directly with primary amines ($-NH_2$).[185] The scheme of carbodiimide crosslinking reaction of N-doped CDs is described in Figure 11.

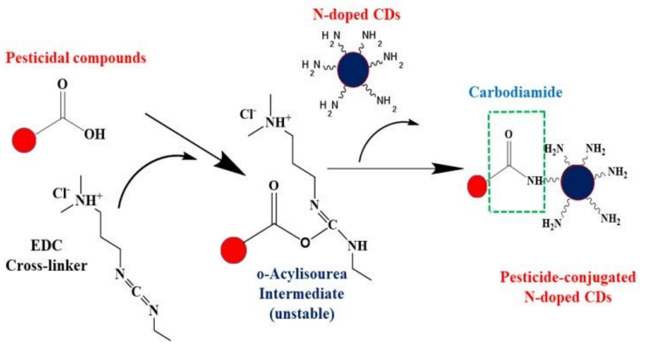

Figure 11 Proposed crosslinking carbodiimide reaction of N-doped CDs for pesticide delivery

This type of carbodiimide conjugate is believed to enhance the efficient use of pesticides and to prolong the release time of pesticides into pests, leading to a long-term pesticidal effect. In other words, it takes time to break the interaction between pesticidal molecules and N-doped CDs, resulting in a slow release rate. The concept of pesticide conjugated N-doped CDs can be described in Figure 12.

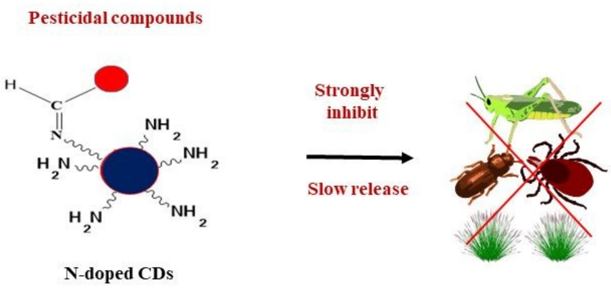

Figure 12 Applications of N-doped CDs as a pesticide carrier for targeting pests

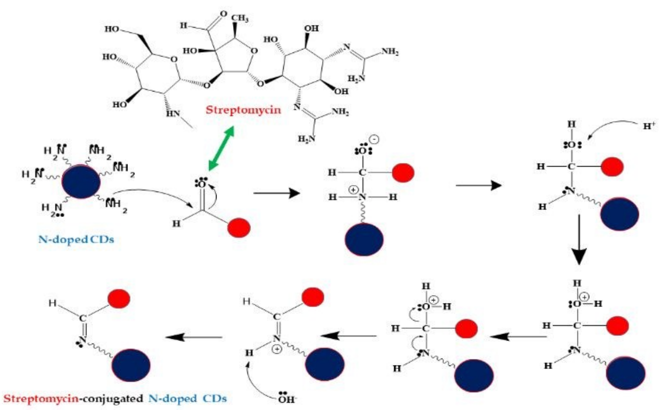

Figure 13 Schematic illustration of conjugation reaction of N-doped CDs with streptomycin

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Table 3. List of antibiotics used to be delivered by N-doped CDs for pest control

Name	Properties	Applications in crop	Ref.
Streptomycin	An aminoglycoside antibiotic, naturally produced by soil actinomycetes	It is used to inhibit the spread of fire blight disease in apples, pears.	188, 189
Gentamicin	An aminoglycoside antibiotic inhibits protein synthesis by binding to the bacterial ribosome.	It is used to inhibit the spread of fire blight disease in apples, pears, and various phytopathogenic diseases caused by species of *Pectobacterium, Pseudomonas, Ralstonia,* and *Xanthomonas*	190
Oxytetracycline (Terramycin)	A naturally produced tetracycline antibiotic of Streptomyces rimosus, with a spectrum of activity similar to chlortetracycline and tetracycline and remarkable thermostability	Control *E. amylovora* on apple and diseases caused by *Pectobacterium spp., Pseudomonas spp.* and *Xanthomonas spp.* on several crops.	189, 191
Oxolinic acid	Oxolinic acid, a synthetic quinolone antibiotic, inhibits DNA replication and consequently bacterial growth.	It is used to inhibit the spread of fire blight disease in apples, pears, and other related plants.	192

Adhesion on leaf and targeting delivery of N-doped CDs to pests depends on the structure of plants and pests. It is reported that the outermost layer of the leaf is called cuticle, which is in direct contact with nanopesticides.[193] On the cuticle surface is a wax layer, which contains long hydrocarbon chains with various functional groups (alkanes, alcohols, aldehydes, and acids).[194] Therefore, the interaction between nitrogen-containing functional groups and the wax layer is significantly enhanced due to the existence of $–NH_2$ groups on the surface of N-doped CDs. As a result, this will lead to spread and adhesion of nanopesticides droplets on plants and pests.[195]

In comparison with other nanocarriers, N-doped CDs have a much smaller particle size with less than 10 nm. [145, 196, 197] Therefore, N-doped CDs with ultrasmall size are easier to penetrate cell membranes of pathogenic fungi, bacteria, and weeds.[198] This new way of delivery through cell membranes makes N-doped CDs more efficient and competitive than conventional pesticide delivery.

The structure of targeted insects is another factor that needs to be considered when designing nanopesticides. It has been known that insect body wall or exoskeleton - the external covering of the body - consists of epidermis and cuticle. The cuticle is the outermost part of the insects' exoskeleton, which includes three sub-layers shown in Figure 14a.[199-201]

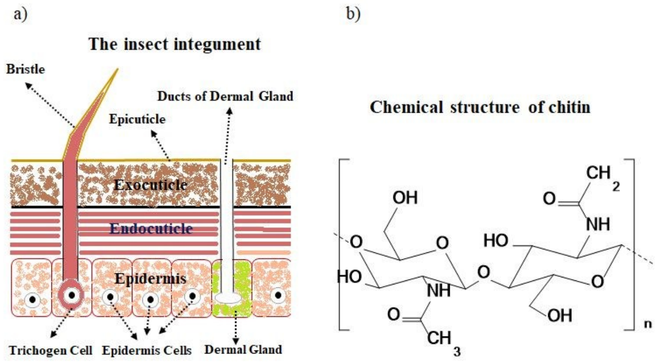

Figure 14 (a) The structure of insects' exoskeleton (insect body wall) in crops. (b) Chemical structure of chitin in insect cuticle

The major component of insect cuticle is nitrogenous polysaccharide and polymer of N-acetylglucosamine, which has been called chitin fibers (Figure 14b).[202] It cannot dissolve in water but become soluble in acids, alkalies, and organic solvents. Chemically, the structure of chitin contains many –OH and –C=O functional groups (Figure 14b), which might have high affinity with N-containing functional groups on the surface of N-CDs. Apart from that, the outer most of epicuticle is made of a non-water-soluble cement layer (wax layer). The composition of this layer varies from insect species such as alkanes, aldehydes, primary alcohols, free fatty acids, esters, and triterpenoids.[203] Therefore, nitrogen-doped nanopesticides like N-doped CDs can enhance their adhesion to insect's exoskeleton due to the interaction of–CHO functional groups on the wax layer with nitrogen-containing groups on N-doped CDs. These morphological and chemical structure of the insect's skeleton will provide an

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enhanced intake of pesticides and also cause other problems, for example, the loss of water from the insect body that will impact their survival in harsh environmental conditions. The enhanced adhesion mechanism of the N-doped CDs on plants and insects is proposed in Figure 15**.** In general, it can be concluded that knowing the precise chemical composition of the exoskeleton and physiological properties of insects would provide a glue for researchers to design the corresponding targeted nanopesticides like N-doped CDs by surface modification.

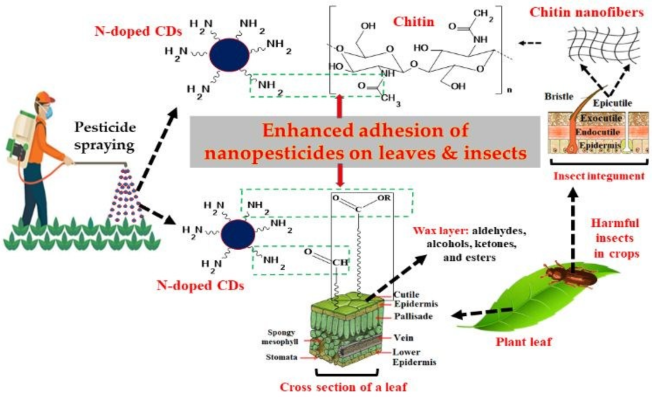

Figure 15 Illustrative sketch of the proposed enhanced adhesion mechanism of N-doped CDs on plants and insects

4. Plasma synthesis of N-doped nanoparticles for agricultural applications

4.1. Principle of plasma synthesis of N-doped nanomaterials

The synthesis of nanomaterials has been of long-standing interest because of their wide range of applications ranging from agriculture, food industry, biomedical and environmental applications to energy. However, and as so general for all nanomaterial syntheses, the effectiveness of their applications is based on their size- and shape-dependent properties. Hence, the production of high-quality nanoparticles with controllable properties becomes indispensable. Consequently, various nanomaterials synthesis methods have been developed, including wet chemical methods,[204] microwave technique,[205] laser ablation,[206] and hydrothermal method.[207, 208] In comparison with the aforementioned conventional methods, plasma synthesis of nanomaterials has recently shown more dominance in terms of generating high-quality nanoparticles because of several reasons. First, plasma technology effectively fabricates or modifies various nanomaterials with less operating processes than conventional methods, hence, significantly reducing the labor costs.[209] The second tremendous benefit of plasma-assisted fabrication and modification system is that prepared nanomaterials possess rich functional groups such as $–NH_2$, -COOH, -CHO, etc. without using any initial chemicals for surface modifications.[210] Lastly, particle size along with morphological, structural, and fluorescent properties of the prepared nanomaterials are adjustable and tailorable.[211]

Plasma has been defined as the fourth state of matter, which can be characterized by complex collective behavior.[211] It contains negatively, positively charged particles, and electrons and free radicals, which can decompose various chemical compounds, and biological components.[212] One of the most significant advantages of plasma treatment or synthesis of N-doped nanomaterials is that they can properly introduce functional groups into the surface of nanomaterials. This benefit can be exploited to dope nitrogen heteroatom with nanomaterials by treating with ammonia or nitrogen gas. In summary, plasma fabrication of N-doped nanoparticles has demonstrated to be a promising technology in pest control. An overall review of N-doped nanoparticles is also performed in Table 4.

4.2. Plasma synthesis of N-doped TiO_2 NPs

Until now, plasma synthesis of N-doped TiO_2 NPs has not been widely applied in agricultural heritage, but it has been used for other applications. Therefore, we will discuss the overall summary of plasma synthesis of N-doped TiO_2 NPs because of their potential applications in pest control that we discussed in the previous sections.

In 2006, a Japanese research group used argon and nitrogen gas to generate plasma for fabricating N-doped TiO_2 particles. This plasma setup is described in Figure 16.[213] In particular, discharge power and discharged time are adjusted in a range from 100 to 400 W, and from 2-20 min, respectively. TiO_2 powders were used as a starting material. The results show that after nitrogen doping, Ti-N bonds are completely formed, which enhance their optical properties in the visible light range**.** From the results, it can be seen that this process is less time-consuming (2-20 min) and more energy-efficient (100 - 400W) without using any toxic additives (only renewable nitrogen gas and argon plasma gas used).

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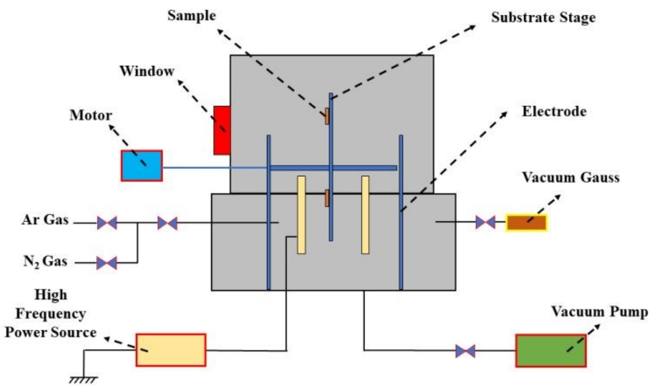

Figure 16 Scheme of the setup of a bell jar-type plasma reactor for N-TiO2 NPs (This figure is adapted from Ref. 213 with permission from the Elsevier, 2006)

In 2007, a novel plasma-assisted fabrication process based on the atmospheric pressure plasma reactor is designed to produce photocatalytic N-doped TiO_2 particles using $Ti[OCH(CH_3)_2]_4$ and water vapors as a source of starting materials, which is shown in Figure 17.[214, 215] The results depicted that the particle size of N-doped TiO_2 photocatalysts is around 22.0 nm. It is also demonstrated that N_2 plasma gas followed by air could generate nitrogen dopants. In this study, $Ti[OCH(CH_3)_2]_4$ and water vapors are used as precursors rather than raw TiO_2 (Figure 16), indicating the flexibility of using starting materials. With a particle size of 22 nm, it reveals that this process can produce well-defined nanoparticles, using non-toxic materials such as N_2, H_2O and $Ti[OCH(CH_3)_2]_4$. Especially, the synthesis process is carried out at atmospheric pressure in a closed system, showing that this system is in high-safety control.

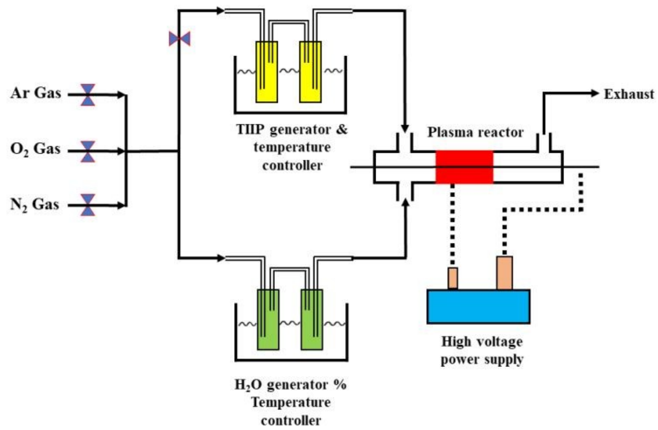

Figure 17 Structure of the plasma-assisted fabrication process based on the atmospheric pressure plasma reactor for generating photocatalytic N-doped TiO2 particles (Reproduced from Ref. 214 with permission from the American Chemical Society 2007)

Table 4. Overall summary of plasma-induced synthesis of N-doped nanomaterials for potential pesticide applications.

N-doped nanopesticides	Typical characteristics	Plasma process	Ref.
N-doped TiO_2	N_2 and Ar plasma	Bell jar-type plasma reactor	213
	N_2 and Ar plasma	Dielectric barrier discharge plasma	214, 215
	Corona discharge in water	Liquid-phase non-thermal plasma	216
	N_2 plasma treatment	RF plasma	217
	H_2 and Ar plasma	Arc discharge	218
	The formation of Arc plasma on the metal surface	Arc plasma	219
N-doped ZnO	N_2 and Ar plasma	DC thermal plasma	220
	Using Ar as a carrier gas	RF thermal plasma	221
N-doped CDs	He plasma	Indirect contact plasma-liquid system	222
	Using acrylonitrile and pyrazine as a source of nitrogen and carbon	Direct contact plasma-liquid system	223
	Using benzene and pyrazine as a source of nitrogen and carbon	Direct contact plasma-liquid system	224

Liquid-phase non-thermal plasma (LPNTP) is another plasma technology that can generate plasma under atmospheric pressure and condition temperature. Plasma at the plasma-liquid interface can promote a complex mixture of reactions in solution. In 2010, LPNTP technology is applied to synthesize N-doped TiO_2 NPs for removal of azo dye (Figure 18).[216] In particular, nanosized TiO_2 and NH_4Cl are used as starting materials. The bipolar pulse is utilized as a power supplier to produce pulsed irradiation in a range from 0 to 30 kV. The frequency rate is set up at 60 Hz with the high voltage discharge electrode (13.5 W), and a high-voltage probe and a pulsed current probe are used to measure the output of voltage and current. The influential parameters of discharge are adjusted and controlled by a digital oscilloscope. To generate a corona discharge in the water phase, an electrode in the form of needle plate is put in the middle

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of a cylindrical quartz tube, and a discharge electrode is made from a stainless-steel hollow needle. The point electrode of the hollow needle is set up in the heart of the cylindrical reactor above the bottom of the vessel. Especially, merely the tip of the point electrode is constructed to contact directly with the water phase. In addition, to make the ground electrode, a stainless-steel round plate is used with a diameter of 40 mm and put at the top of reactor opposite to needle-like discharge electrode. The temperature is modified in a range from 273 to 323 K with the airflow rate of 150 mL/min. The results show that this system is energy-efficient (13.5 W) in high safety control (a closed system at low temperature).

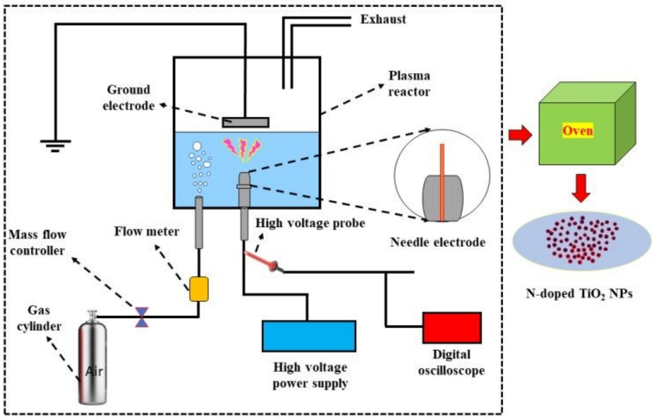

Figure 18 Schematic drawing of the liquid-phase non-thermal plasma (LPNTP) system (This figure is adapted from Ref. 216 with permission from Water Science and Technology 2010)

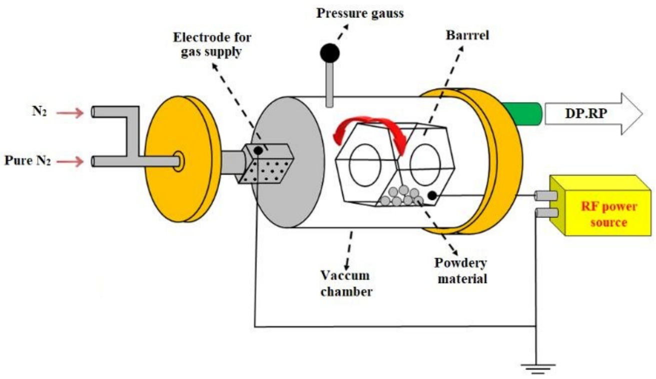

Figure 19 Scheme of the plasma treatment system to fabricate N-doped TiO2 (This figure is adapted from Ref. 217 with permission from the Elsevier, 2012)

In Figure 19, the plasma-assisted system is developed and combined with the particle-stirring system relied on the polygonal barrel-sputtering method to generate N-doped TiO_2.[217] This system includes an electrode for the gas-supply and a vacuum chamber with a hexagonal barrel. N_2 gas is used to generate plasma for N-doped TiO_2 synthesis in a range of time from 30 to 180 min, radio frequency (RF) is used as a power supply with a power of 25–300 W and frequency rate of 250 kHz. The results indicate that treatment time, the RF power, and gas pressure directly influence on the absorbance in visible light range and the amount of nitrogen in plasma. It can be concluded that this system is a closed system with high-safety control and energy efficiency.

Another research group also developed a plasma system based on the arc-discharge method for mass production of N-doped TiO_2 NPs.[218] In particular, a pure titanium-made cylinder is set as the anode, and a tungsten needle is used as the cathode. The results depicted that most N-doped TiO_2 NPs show a disordered surface layer with 5 nm in thickness.

In 2018, a novel plasma-assisted fabrication of N-doped TiO_2 NPs is developed based on electrolysis method using bulk titanium (Ti) as source material and nitric acid as a nitrogen source (Figure 20).[219] During the plasma-induced synthesis process, gaseous anionic species are generated to react with cationic Ti species to form N-doped TiO_2 NPs due to the formation of arc plasma on the metal surface. In this system, bulk titanium (Ti) is used as a source material, compared to other materials like commercial TiO_2 or $Ti[OCH(CH_3)_2]_4$, indicating that plasma synthesis of N-doped TiO_2 is flexible about using of starting materials.

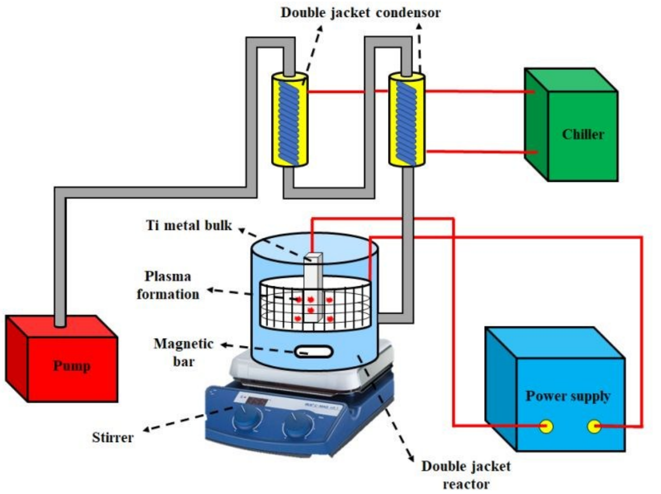

Figure 20 Illustration of plasma-assisted fabrication based on electrolysis for N-doped TiO2 NPs (This figure is adapted from Ref. 219 with permission from the Elsevier, 2018)

4.3. Plasma synthesis of N-doped ZnO NPs

Similar to the N-doped TiO_2 NPs, various studies on plasma synthesis of N-doped ZnO NPs have been developed. A novel dc thermal plasma reactor is designed to synthesize N-doped ZnO NPs with an average particle size of 31 nm.[220] Figure 21 expressed the plasma synthesis reactor of N-doped ZnO NPs based on dc thermal plasma technology. As a result, the adsorption of photocatalytic ZnO NPs under irradiation is obtained by doping several thousand ppm of nitrogen into ZnO. It is also demonstrated that N-doped ZnO NPs exhibit strongly photocatalytic decomposition of methylene blue and antimicrobial activity under visible light exposure. Once again, this result shows the potential applications of N-doped ZnO NPs in agricultural heritage. The power of the dc plasma-based reactor is determined at 70 kW under atmospheric pressure. The primary source of material is ZnO powders with a mean particle size of 10 µm. To dope nitrogen into ZnO particles, nitrogen gas is introduced into the plasma-forming and carrier gasses.

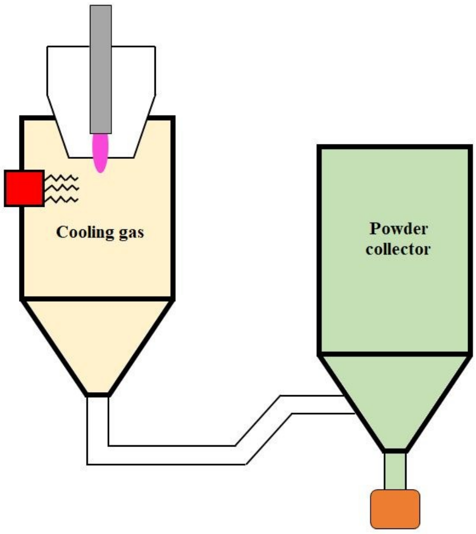

Figure 21 Plasma synthesis reactor of N-doped ZnO NPs based on dc thermal plasma technology TiO2 (This figure is adapted from Ref. 220 with permission from the Elsevier, 2012)

In 2016, a RF thermal plasma process is introduced to produce massively N-doped ZnO NPs.[221] The scheme of the RF thermal plasma-assisted synthesis of N-doped ZnO NPs is described in Figure 22. First of all, the gas used to generate plasma is transferred to the torch, with the cooling water system. Later on, RF power is supplied to the induction coil. After introducing an electromagnetic field into the torch, the thermal plasma is formed. Finally, the precursors, along with carrier gas, are supplied to the thermal plasma to process vaporization and reactions. The fabrication conditions of the prepared N-doped ZnO NPs are adjusted to the power of 30 kW, with the frequency at 3.5 MHz, and the pressure at 150 Torr. The cooling system is used to keep the temperature of the reactor's wall always at 300 K. The starting materials to be fed into the plasma flame are Zn powders. The results demonstrated that this system can perform massive production of N-doped NPs.

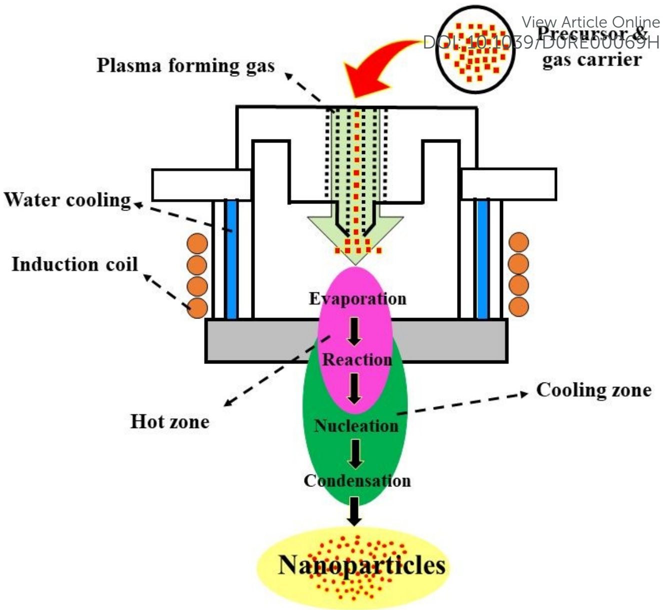

Figure 22 Schematic procedure of the RF thermal plasma for the synthesis of N-doped ZnO NPs TiO2 (This figure is adapted from Ref. 221 with permission from the Elsevier, 2016)

4.4. Plasma synthesis of N-doped CDs

In spite of being discovered in the last decades, N-CDs become one of the most advanced materials, which can be used for various applications. For this reason, many different fabrication methods have been tried to produce high quality N-doped CDs. Recently, the microplasma system has shown its significant advantages in the production of N-doped CDs. Plasma-assisted nitrogen doping can also take place either in the form of indirect contact plasma-liquid (ICPL) system or the direct contact plasma-liquid (DCPL) system due to the high flexibility of the plasma configuration. ICPL refers to the setting where plasma is generated in the gas phase above the surface of the electrolyte solution, while DCPL refers to the setting where plasma is formed within the bulk liquid volume.

Microplasma under atmospheric pressure generated in the form of ICPL is used to produce N-doped CDs with citric acid (CA) and ethylenediamine (EDA) as starting materials [222]. The microplasma synthesis procedure of N-doped CDs is shown in Figure 23. Typically, a given amount of citric acid (CA) and ethylenediamine (EDA) are used to dissolve in deionized water. Later on, a microplasma produced by a DC power under atmospheric pressure is set above the surface of the solution. The microplasma treatment is set up for 30 minutes as the anode, while the discharge current and discharge voltage are continuously kept at 6 mA and 13 kV, respectively.

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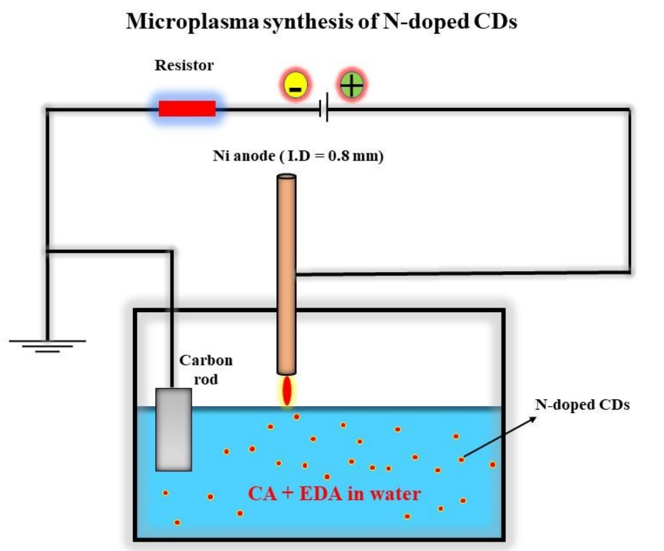

Figure 23 Indirect microplasma–liquid interaction synthesis of nitrogen-doped carbon dots (N-doped CDs) from citric acid and ethylenediamine as initial precursors in water. (This figure is from Ref. 222 with permission from the Royal Society of Chemistry)

Regarding DCPL, the addition of plasma gas is not necessary. Two types of the most well-known electrodes are pin-to-pin and pin-to-plate geometries. High voltage pulses are usually utilized to generate plasma as the corona. In Figure 24, a solution plasma process is introduced to produce N-doped CDs using acrylonitrile and pyrazine as a precursor source.[223] Notably, approximately 100 mL of the solution of starting materials is used for solution plasma treatment. Microplasma treatment time is set about 20 min under stirring. A tungsten wire is protected by a ceramic tube and designed as the electrodes with a diameter of 1 mm. In the middle of a glass reactor, there is a pair of tungsten electrodes with a gap distance of 0.5 mm. A bipolar high voltage pulse with an intensity of 2.0 kV is applied to the tungsten electrodes, and the frequency is set at 20 kHz.

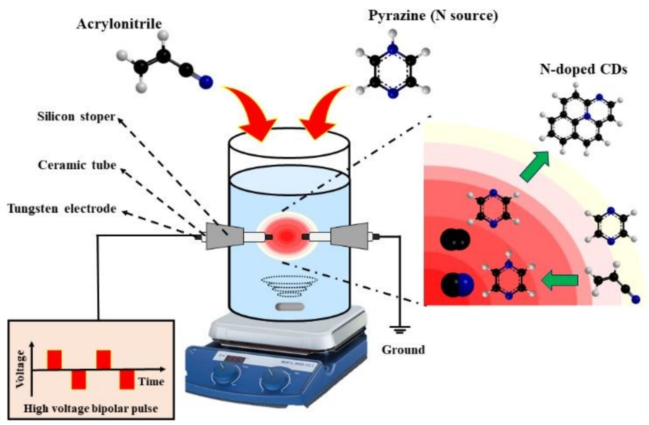

Figure 24 Direct contact plasma-liquid (DCPL) system for the synthesis of N-doped CDs (This figure is from Ref. 223 with permission from the Royal Society of Chemistry)

Similarly, another study has been also conducted to fabricate N-doped CDs (Figure 25), but the precursor sources for the synthesis are benzene and pyrazine.[224] In particular, a tungsten wire with a diameter of 1 mm is designed as the electrodes, and shielded by a ceramic tube. In the middle of a glass reactor, a pair of tungsten is set with a distance of 1 mm. The intensity of the bipolar high voltage pulse used to apply to the tungsten electrodes is 1.5 kV, and the repetition frequency is adjusted to 20 kHz. The starting materials to synthesize N-doped CDs are benzene and pyrazine. Microplasma is introduced into 100 mL of the mixed starting materials under vigorous stirring for 20 min. When the microplasma is produced in between the electrodes, N-doped CDs is formed.

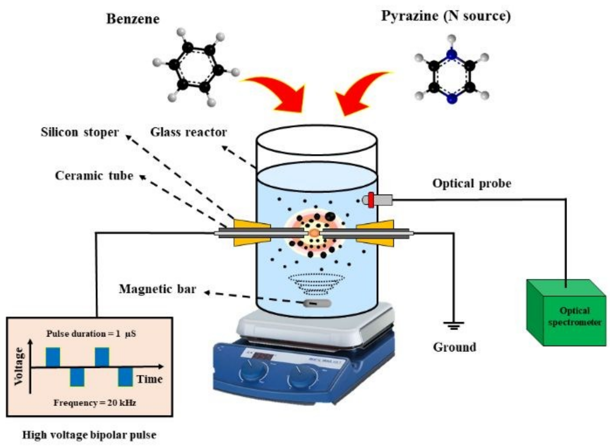

Figure 25 Schematic illustration of the experimental setup for solution plasma synthesis of N-doped CDs (This figure is from Ref. 224 with permission from the Royal Society of Chemistry)

5. Green plasma-assisted production of N-doped NPs as a part of the "Agri-tech Revolution"

Global warming,[225] degraded cultivating land,[226, 227] and pesticide-resisted phytopathogens due to overuse of pesticides[228] are primary causes of crop loss, leading to a remarkable decrease in biodiversity and impairment of ecosystem functions needed for green agro-ecosystem.[229] With an alarming rate of population escalation, it has been estimated that the world's population has reached 7.7 billion in 2019, and is predicted to increase by more than 2 billion in 2050.[22] Therefore, an increase by 50 - 80 % of crop production is estimated for food demand and agriculture-based products by 2050.[230] Besides that, the lack of water resources and global spread of phytopathogens are other factors that lead to deterioration of current green agro-ecosystem.[230]

Based on such urgent needs and threats, a new agri-tech revolution has been recently proposed[19] with the aim of sustaining effective and

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efficient crop production to meet the demand of food in the future. This revolution, which is triggered by the advancement of information technology, novel materials, methods, and the use of plant-growth-promoting bacteria,[231] has potential advantages to make an improvement toward a more effective, efficient, resilient, green, sustainable agro-ecosystem.[19]

For many decades already the so-called "green revolution"[19] has brought considerable benefits for the N-nitrogen fixation by advancing the Haber-Bosch (H-B) process, mechanization, agricultural irrigation, agrochemicals, etc.[19] Chemical nitrogen-fixation by H-B process has played the crucial role in the green revolution and actually initiated it (Figure 26). These technological advancements have led to considerably improved crop production efficiency. Nonetheless, the environmental impact has risen significantly from 1920 to 2020. This makes clear that the green revolution alone cannot meet the demand for sustainability in the future, due to the dynamics of the above-mentioned population growth and its assorted environmental burdens.[19] Rather, a declining resilience, increasing environmental damage, and increasing environmental impact is predicted, if simply moving on as in the past (Figure 26). Consequently, this indicates that the green revolution may come to an end.

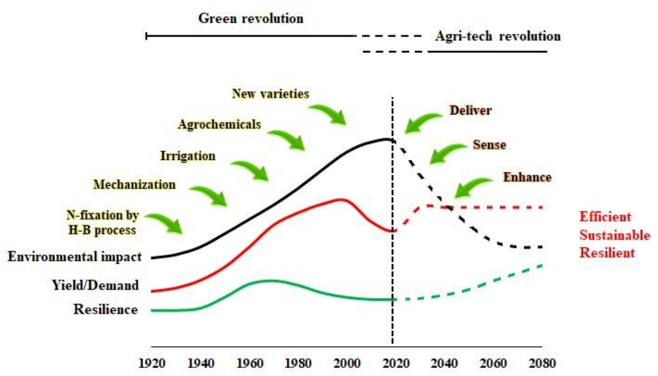

Figure 26 Overall scheme of the green revolution and the new agri-tech revolution (This figure is from Ref. 19 with permission from Nature 2019)

An entire new approach is needed, the agri-tech revolution as defined above, to increase crop yields and resilience, and to lessen the environmental impact. Its integral parts are the targeted delivery of pesticides, phytopathogenic detection, enhanced management of plant diseases (Figure 26). To the best of our knowledge, engineered nanomaterials (ENMs) are an excellent approach to meet those requirements. We have given evidence for that in this review: N-doped NPs are introduced and proven to be potential ENMs for enhancing crop production, also reducing the environmental effect. Existing industrial technology, including the ever-improving H-B process, will play its role in the agri-tech revolution. Yet, there is clearly a demand for alternative green technologies as well, and if it is only for reasons of complementary market provision, and that is why plasma-based nitrogen fixation has been introduced in this review.

In the following, the greenness of the technology will be illustrated through four categories: (i) resource/waste on a reaction level, (ii) starting-material flexibility on a process level which translates to product flexibility, (iii) performance on a functional materials level, and (iv) process safety on a process level.

Seen from a resource/waste perspective, the plasma synthesis of N-doped NPs provides access to abundant, green, "renewable atmospheric nitrogen" as precursors. This plasma technology is also a simple process, meaning that nitrogen can be easily fixed on the surface on nanoparticles without using any additive chemicals. The solvent itself can be used as starting materials[222-224] (see above for the solvents); which essentially makes the reaction "solvent (waste)-free".

Seen from a process-to-product perspective, there has given indication in the section 4 that the plasma manufacture of N-doped NPs is a flexible process in term of starting materials utilization. In particular, starting materials can be used in liquid, solid, or gas phase, allowing a diversity of designs of ENMs to meet specific agricultural applications (e.g. delivery of pesticides, phytopathogenic detection, enhanced adhesion of pesticides etc.). To synthesize N-doped CDs, for example, starting carbon materials could be in the liquid phase,[222] reacting with nitrogen-containing gas in the plasma phase. As a process variant and to increase the nitrogen doping content in N-doped CDs, precursors could be selected from various mixtures of nitrogen and carbon sources such as benzene and pyrazine[222], citric acid and ethylenediamine,[223] acrylonitrile and pyrazine. [224] There is also evidence showing that N-doped CDs can be synthesized from gaseous carbon based-precursors. Another process variant may use solid precursors such as for N-doped TiO_2 NPs. Specifically, bulk titanium (Ti) was used as a solid starting material. During the plasma-induced synthesis process, gaseous anionic species are generated to react with cationic Ti species to form N-doped TiO_2 NPs due to the formation of arc plasma on the metal surface (Figure 20).

Seen from a performance/function perspective, a noticeable learning from the section 4 is that the plasma-assisted nitrogen fixation process has the potential to synthesize and modify high-quality engineered nanoparticles, especially N-doped NPs as nanopesticides. Those advanced materials largely fulfill the requirements part of the agri-tech revolution such as maximal use of starting materials, renewable precursors, reduced carbon footprint, energy efficiency,

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minimal toxicity to human, maximal process safety, minimal solvent load, minimal waste, and flexible precursors.

Seen from a process safety perspective, the plasma-assisted synthesis of N-doped NPs is carried out in a closed system (reactor) at ambient conditions, which maximizes safety control as well as reduce unexpected accidents related to safety control.

To summarise, the plasma-based production of N-doped NPs has potential to maximize the use of renewable precursors, minimize waste production into environment and solvent load, as well as lessen toxicity and carbon footprint to human and environment due to no toxic additives used or released. In addition, it fulfils the demands of the resilient and sustainable agri-tech revolution such as energy-effectiveness/carbon emission, high quality and quantity production, and maximal safety control. Finally, there is a quality argument. With its flexible designs, the plasma-assisted production enables to produce a high quality N-doped NPs with material properties fine-tuned to the purpose.

6. Conclusions

This review paper has studied and proved the recent achievements on using green plasma-based technology, compared to other conventional methods, to fabricate N-doped NPs and the pesticidal applications of these nanomaterials in pest control. Various plasma-assisted synthesis methods have been developed to fabricate N-doped NPs. The unique physiochemical characteristics of plasma-induced fabrication introduced active nitrogen species into the surface of nanoparticles (nanopesticides), which results in nitrogen-doped NPs. The existence of nitrogen heteroatoms on their surface also enhances intrinsic properties of these nanopesticides, leading to potential multifunctional applications in agriculture such as pesticide nanocarriers, nanopesticides, phytopathogenic detection, and phytopathogen targeting. Some evidence has been given to prove the antibacterial and antifungal activities of N-doped NPs, paving a way for these nanomaterials to apply widely in pest control. More importantly, plasma-induced synthesis is a flexible approach as to develop various N-doped nanoparticles for targeting specifically harmful phytopathogens when chemical structure, biological, and physiological properties of these targeted pathogenic microorganisms are thoroughly understood. Finally, plasma-assisted production of N-doped NPs is considered as a part of new agri-tech revolution because of their potential advantages for maximal use of starting materials, renewable precursors, reduced carbon footprint, energy efficiency, minimal toxicity to human, maximal process safety, minimal solvent load, minimal waste, flexible precursors.

7. Outlook

In this review, perspectives of promising applications of N-doped NPs as emerging nanopesticides and their synthesis using plasma-enabled NP technology as a green and eco-friendly and sustainable approach is presented. Several examples of N-doped NPs such as N-doped TiO_2 and N-doped ZnO evidently shows their promising potential for development of new generation of nanopesticides based on their unique nanoscale size and active cites, catalytic performances, and new mode of pesticidal actions action. Plasma-assisted synthesis of N-doped NPs to produce these materials in future has been reviewed as an advanced technology due to its green, facile, low-cost and industry scalable capabilities. The presence of free radicals, negatively and positively charged ions in plasma is the primary reason that makes plasma-based fabrication method suitable for N-doped NPs synthesis. In comparison with traditional methods, this technique has potential to improve nanopesticides production in the light of several reasons as follow:

(1) Plasma induced synthesis generate fine N-doped nanoparticles under atmospheric pressure and condition temperature.

(2) Multi-steps of fabrication can be eliminated, leading to a more straightforward procedure without using addictive chemicals for conjugation.

(3) Safety and hazard conditions are concerned in this system as influential parameters are controllable.

(4) Plasma-generated N-doped NPs are eco-friendly and easy-to-produce nanomaterials and can be widely and effectively applied for cultural heritage.

The success of using plasma technology to produce high quality multifunctional nanopesticides will provide new opportunities for pest control in industrial scale. In order to deliver multifunctional NPs to large-scale agricultural production, our vision is to use smart spreaders. This seems to be a viable option, because spraying can deliver a pesticide over a large area. Due to the high pesticidal activity, targeted spraying systems can be employed for efficient dosing of chemical (low concentration) and thus allow operation at low cost. In addition, multifunctional nanopesticides will be delivered in the form of suspension to the plants. As we discussed in the review paper, due to the advantaged of plasma to modify the surface of

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ultra-small nanopesticides with –COOH –OH groups, which make it more water dissolvable. Therefore, these nanopesticides are easily to be dissolved in the form of suspension. The application of the new functionalized NPs in the have been indeed shown promising for the propagation in the field/greenhouses. For example, Mohammad et al. (2013) reported that magnetite nanoparticles were used in a greenhouse in order to investigate the impact of these functionalized NPs on Soybean chlorophyll. [232]

However, in order to commercialize these pesticidal products, environmental and health risk assessment of these nanopesticides should be carried. Unlike conventional pesticides, nanopesticides need a different approach for risk assessment (Rai S. Kookana et al., 2014).[233] The Organisation for Economic Co-operation and Development (OECD) runs a large work program that is considering how test guidelines may need to be adapted in order to assess the hazard of nanopesticides. The particle number concentration and particle size distribution (PSD), as well as the ratio of "free" and nanoparticle-bound artificial intelligence are proposed for the determination of the pesticide bioavailability and toxicity. Approaches that are used to evaluate and reduce the NP health hazard could include scattering methods (e.g., DLS), particle tracking methods (e.g., NTA), centrifugal methods (e.g., DCS), or fractionation methods (e.g., FFF), the latter method allowing for determination of ai size when coupled with appropriate chemical selective detectors.

Although plasma-assisted synthesis of N-doped nanoparticles as nanopesticides are demonstrated as a promising technology, there are still some issues that needs to be addressed. For instance, the influential parameters on synthesis conditions should be optimized depending on properties and structure of N-doped NPs such as the design of plasma reactor, types of plasma, precursor sources, types of power supply, etc. Mechanisms N-doped NPs as nanopesticides in inactivating various pathogenic bacteria and fungi are still unanswered. Laboratory-scale plasma production of N-doped NPs has been successfully demonstrated, while industrial production for large-scale agricultural applications is also a challenge for future development.

In the long-term strategy, estimating the production cost needs to be considered as it plays a key point to further develop plasma production of nanopesticides in a large scale. Therefore, this is the main challenge for further development of plasma-assisted synthesis of N-doped nanoparticles as nanopesticides in pest control.

To our best knowledge, there are no cost studies on the feasibility of a commercial manufacturing of nanopesticides. Yet, an analogy can be drawn to the commercial exploitation potential of plasma-based N-fixation processes for the manufacture of fertilisers, reported by us in the last years. [234, 235] Anastasopoulou et al. have conducted a series of techno-economic feasibility studies on the plasma-based fertiliser production, as an outcome of the industry-driven MAPSYN (Microwave, Ultrasonic and Plasma assisted syntheses) European project. [234- 240] These studies revealed that plasma-based fertiliser production of nitric acid, under the best assumptions (recycling, energy recovery), could have a better environmental profile than the conventional process. [234] In terms of energy resources, the plasma-assisted fertilizer production is efficient in incorporating (local) renewable power supplies (solar, wind, etc.). The sustainability benefit of such green-energy powered plasma-based fertiliser production has been quantified compared to conventional natural gases. The Global Warming Potential value is improved in the range of 68% – 91% with respect to lignite–based energy supply. [234] Additionally, in terms of production process scale, the results showed that a 10 ton per day (t/d) plasma-assisted fertilizer production plant operated at 6% NO yield and with an energy consumption of 1396 KW per day. [235]

Motivated by this, a compact-plant ('container') based local fertiliser manufacture at the site of agricultural production has been envisioned ('Fertilising with the Wind', Evonik Company). The LEAP-Agri project AFRICA from the European Union aims currently to bring such plasma technology to Africa on a small pilot scale. [241]

Apart from the aforementioned advantages, capital costs and energy costs are not yet in the range of a good industrial process. [238] For example, a plasma-assisted fertilizer production plant (10 t/d, with 6% NO yield) using the local solar and wind energy resources in Kenya would cost up to 155 and 312 million $, respectively.[235] Plasma-made nitric acid is calculated to be about 4 times more costly than conventionally made in terms of life-cycle costs.[239] As for electricity sold, this fertilizer plant will consume 10,155,706 (solar energy) and 21,720,846 (wind energy) kWh/year. [235]

It is hoped that this review could provide an insight into a novel plasma-assisted synthesis of N-doped NPs and the applications of these multifunctional NPs for agricultural pest control, paving a new way for more efficient, sustainable and environmental-friendly agriculture.

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Conflict of Interest

The authors declare that they have no conflict of interest.

Contribution

Mr. Hue Quoc Pho wrote and edited the draft of manuscript. Prof. Volker Hessel, Prof. Dusan Losic, Prof. Kostya (Ken) Ostrikov, and Dr. Nam have revised the draft.

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