农药学学报 2024, 26(3): 415-426
*Chinese Journal of Pesticide Science*
http://www.nyxxb.cn
E-mail: nyxuebao@263.net

•专论与综述•
**doi**: 10.16801/j.issn.1008-7303.2024.0029

# 功能化纳米农药载药系统研究进展

刘慧慧[1]， 申 越[1]， 李兴业[1]， 李柠君[1]， 王心悦[1]，
安长成[1]， 吴青君[2]， 王 琰[*,1]

(1. 中国农业科学院农业环境与可持续发展研究所，北京 100081；2. 中国农业科学院蔬菜花卉研究所，
蔬菜生物育种全国重点实验室，北京 100081)

**摘 要**：纳米材料因其粒径小、尺寸易调节、种类丰富以及良好的移动性等优势，作为有效载体，在农药载药系统及农业病虫害防治方面受到了广泛关注。纳米材料与技术在提升农药生物利用度、溶解性和缓控释特性等方面展现出巨大的潜力。本文总结了利用纳米材料与技术开发具有功能化纳米农药载药系统的研究进展，系统综述了精准释放农药活性成分的智能响应型农药控释制剂、叶面亲和型、土壤用药型及农药双载体系等不同功能化纳米农药载药系统，概述了其在农药减量增效和精准施用方面的作用效果，并对功能化纳米农药载药系统的应用场景与产业化潜力进行了展望。

**关键词:** 纳米农药；纳米载药系统；控释，智能响应；双载体系
**中图分类号**：TQ450.6 **文献标志码**：A

# Research progress of functional nano pesticide carrier systems

LIU Huihui[1], SHEN Yue[1], LI Xingye[1], LI Ningjun[1], WANG Xinyue[1],
AN Changcheng[1], WU Qingjun[2], WANG Yan[*,1]

(1. *Institute of Agricultural Environment and Sustainable Development*, *Chinese Academy of Agricultural Sciences*, *Beijing* 100081, *China*;
2. *State Key Laboratory of Vegetable Biobreeding*, *Institute of Vegetables and Flowers*, *Chinese Academy of Agricultural Sciences*, *Beijing* 100081, *China*)

**Abstract:** Duo to their advantages of small particle size, easy size adjustment, rich diversity and good mobility, nanomaterials have attracted wide attention as effective carriers in pesticide delivery systems and agricultural pest control. Nanomaterials and technologies have shown great potential in improving the bioavailability, solubility and slow-release properties of pesticide formulations. This paper summarized the research progress in the development of functional nanopesticide delivery systems using nanomaterials and technologies, systematically reviewed the intelligent-responsive pesticide controlled-release formulations that accurately release pesticide active ingredients, and different functional nanopesticide delivery systems such as leaf affinity, soil adsorption and pesticide dual loading systems. The effects of nanopesticide delivery system on pesticide reduction, efficiency

收稿日期：2023-10-13；录用日期：2024-02-25；网络首发日期：2024-04-01.
**Received:** October 13, 2023; **Accepted:** February 25, 2024; **Published online:** April 1, 2024.
**URL:** https://doi.org/10.16801/j.issn.1008-7303.2024.0029
http://www.nyxxb.cn/cn/article/doi/10.16801/j.issn.1008-7303.2024.0029
基金项目：国家重点研发计划项目 (2022YFD1401200).
**Funding:** Supported by National Key Research and Development Project (No. 2022YFD1401200).
第一作者 (First author)：刘慧慧，E-mail：82101222092@caas.cn. *通讯作者 (Corresponding author)：王琰，E-mail：wangyan03@caas.cn.
The authors declare that they have no competing interests.

enhancement and precise application were summarized, and the application scenarios and industrialization potential of functional nanopesticide delivery system were prospected.

**Keywords:** nanopesticides; nano carrier systems; controlled-release； smart response; double-loaded system

## 0 引言

纳米材料是指至少一维在纳米尺度 (1~100 nm) 范围内或由此为基本单元构成的材料[1-2]。纳米材料因其粒径小、尺寸易调控、比表面积大以及独特的物化性质[3]，在改良农药制剂、创制纳米农药新制剂方面展现出巨大的发展潜力，给农业病虫害绿色防控带来了新策略[4-5]。近年来，已有大量研究表明，利用纳米材料与技术构建纳米农药载药系统能有效解决传统农药利用率低、生物利用度差、不稳定等问题[6-9]。纳米农药有诸多优点[10] (图 1)：能够有效增加药液在作物叶面的覆盖率及与害虫的接触面积，增强药液的靶向沉积效率[11]；利用亲水或亲油性纳米载体还可以对药液表面进行叶面亲和性修饰，促进载体材料与作物叶面微纳结构相互作用，使药液更大程度地沉积黏附在叶面上，减少施药时药液的飞溅、流失，具有抗雨水冲刷的能力；结合农药应用场景，纳米材料与技术还能对农药进行功能化调控，实现农药活性成分的长效释放，构建具有不同响应机制的智能控释系统，能使农药活性成分在特定响应场景以一定速度精准释放，极大地提高农药利用率、减少农药施用量。

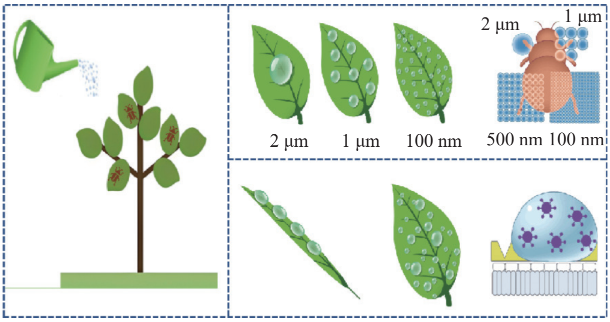


**图 1 纳米农药有效提高农药生物利用度和防治效率**

**Fig. 1 Nano-based pesticide effectively improved pesticide bioavailability and control efficiency**

目前，纳米农药的合成途径有两种[12]：一是农药纳米化，即利用机械破碎等纳米加工技术对农药原药进行加工，通过表面活性剂等助剂的调配，形成稳定的纳米乳、纳米悬浮剂、纳米固体分散剂等剂型[13]；二是农药载体纳米化，即利用纳米材料负载农药，通过封装、吸附、包埋等方式与农药活性成分有效结合构建纳米农药载药系统[14]，如纳米微胶囊、纳米微球等。纳米材料自身结构、尺寸、表面电荷和官能团性质对纳米农药载药系统的构建至关重要[15]。常用的纳米材料包括天然高分子材料、无机硅材料、碳基材料等生物相容性材料[16-18]，如明胶、海藻酸钠、纤维素、聚乳酸、*β*-环糊精、壳聚糖、层状双氢氧化物、介孔二氧化硅、量子点、单壁碳纳米管等[16-22]。根据不同纳米材料结构特性，多种纳米载药系统制备工艺得到了完善，包括喷雾干燥法、溶剂蒸发法、界面聚合法、原位聚合法及膜乳化法等[23-28]。随着纳米技术的迅速发展，越来越多学者关注纳米载药系统的研究，本文主要从功能性出发，针对智能响应型、叶面亲和型、土壤用药型及双载体系等纳米载药系统的研究进展进行了综述，旨在为后续纳米载药系统的研究与发展提供理论基础。

## 1 纳米农药智能响应型控释系统

缓释技术在 20 世纪 70 年代被研究人员发现并应用于农药领域，能有效改善农药持效期短、稳定性差的问题[29-30]，通过基质对农药活性成分的包埋、吸附，实现农药活性成分缓慢释放，如微胶囊悬浮剂等。然而传统农药缓释剂在释放农药活性成分时主要通过被动扩散、解析、胶囊破裂等方式，造成农药释放不均、易受外部环境影响、释放速度难控制、释放效果不好等问题[31]。如果能实现农药活性成分控制释放，构建以适应环境变化的控释制剂，其控释机制结合作物生长特性、病虫害发生规律进行精准持续释放，并保证释放量高于病虫害田间防治有效剂量，则能够充分发挥农药作用效果[32]，有效控制农业病虫害，保障作物健康[33]。因此开发环境响应型纳米控释系统是改善传统缓释剂，促进农药活性成分智能控制释放的新策略。近年来，农药控释技术不断地朝着精准化、智能化和可调控的方向发展，利用温敏、湿敏等响应材料负载农药活性成

分，构建具有智能控释和响应功能的环境响应型纳米农药载药系统，能够有效实现农药精准靶向释放，使农药释放机制与病虫害发生规律相吻合，充分发挥药物的防治效果，极大地提高农药利用率。纳米农药智能响应控释系统根据响应机制不同，可以分为 pH 响应、光响应、温度响应、酶响应和氧化还原响应等。其中 pH 响应研究占 37%、其次是光响应占 27%、温度响应占 17%、酶及氧化还原等其他响应刺激占 19%[34]。纳米农药智能响应控释系统主要是通过载体材料的官能团修饰、特异性结构变化等，针对不同触发因子，实现农药活性成分的释放。因此，不同载体材料及触发器可以产生多种响应机制，响应不同的环境条件，如表 1 所示。

**表 1　不同纳米农药智能响应控释系统的构成及响应条件**

**Table 1　Structure and response conditions of intelligent response controlled release system of different nano pesticides**

| 响应机制 Responding mechanism | 纳米材料/载体材料 Nanomaterial/ Carrier material | 响应触发器 Response triggers | 农药 Pesticide | 参考文献 Reference |
|---|---|---|---|---|
| pH | 介孔二氧化硅 Mesoporous silica | 甲基丙烯酸缩水甘油酯-丙烯酸聚合物 Glycidyl methacrylate-acrylic acid polymer | 阿维菌素 abamectin | [35] |
| | ZnO@ZIF-8 | ZnO | 小檗碱 berberine | [36] |
| | 介孔二氧化硅 Mesoporous silica | 多巴胺 Dopamine | 嘧菌酯 azoxystrobin | [37] |
| | 介孔二氧化硅 Mesoporous silica | ZIF-8 | 咪鲜胺 prochloraz | [38] |
| | 介孔二氧化硅 Mesoporous silica | 多巴胺 Dopamine | 毒死蜱 dursban | [39] |
| | 双峰介孔二氧化硅 Bimodal mesoporous silica | 聚甲基丙烯酸/$Fe^{3+}$ Molymethacrylate /$Fe^{3+}$ | 咪鲜胺 prochloraz | [40] |
| | 多孔碳酸钙 Porous calcium carbonate | 金属酚醛树脂 Metallic phenolic resin | 咪鲜胺 prochloraz | [41] |
| 光 Photo | 二氧化硅 Silicon | 肉桂酸 Cinnamic acid | 二甲戊乐灵 pendimethalin | [42] |
| | 苝-3-基甲醇 Perylene 3-carbinol | 荧光 Fluorescence | 2,4-二氯苯氧乙酸 2,4-dichlorophenoxyacetic acid | [43] |
| | 生物炭@氨基硅 Biochar@aminosilicon | 偶氮苯 Azobenzene | 草甘膦 glyphosate | [44] |
| | 葫芦脲 Cucurbituril | 偶氮苯 Azobenzene | 百草枯 paraquat | [45] |
| 温度 Temperature | 水凝胶 Hydrogel | 聚 *N*-异丙基丙烯酰胺 Poly *N*-isopropylacrylamide | 高效氯氟氰菊酯 *lambda*-cyhalothrin | [46] |
| | UIO-66 | 聚 *N*-异丙基丙烯酰胺 Poly *N*-isopropylacrylamide | 茚虫威 indoxacarb | [47] |
| | 介孔二氧化硅 Mesoporous silica | 聚 *N*-异丙基丙烯酰胺-甲基丙烯酸 Poly *N*-isopropylacrylamide-methacrylic acid | 噻虫嗪 thiamethoxam | [48] |
| | 脂质体纳米囊泡 Liposome nanovesicle | 脂肪酸 Aliphatic acid | 甲维盐/ 烯啶虫胺 metretinate/ endinium | [49] |
| | 介孔硒纳米粒子 Mesoporous selenium nanoparticle | 琼脂糖 Agarose | 异菌脲 iprodione | [50] |
| 酶 Enzyme | 二氧化硅 Silicon | 脲酶 Urease | 二甲戊乐灵 pendimethalin | [51] |
| | 介孔二氧化硅 Mesoporous silica | 果胶酶 Pectase | 咪鲜胺 prochloraz | [52] |
| | 中空介孔二氧化硅 Hollow mesoporous silica | $\alpha$-淀粉酶 $\alpha$-Amylase | 阿维菌素 abamectin | [53] |
| | 中空介孔二氧化硅 Hollow mesoporous silica | $\alpha$-淀粉酶 $\alpha$-Amylase | 阿维菌素 abamectin | [54] |
| 双响应 Dual response: pH/酶 pH/Enzyme | UIO-66 | 草酸/纤维素酶 Oxalic acid/cellulase | 吡唑醚菌酯 pyraclostrobin | [40] |
| | 空介孔二氧化硅 Hollow mesoporous silica | 酸性/纤维素酶 Acid/cellulase | 吡唑醚菌酯 pyraclostrobin | [55] |
| | 中空介孔二氧化硅 Hollow mesoporous silica | 碱性/$\alpha$-淀粉酶 Alkaline/$\alpha$-amylase | 茚虫威 indoxacarb | [56] |
| | 聚多巴胺 Polydopamine | 碱性/脲酶 Alkaline/ urease | 阿维菌素 abamectin | [57] |
| | ZIF-8 | 酸性/$\alpha$-淀粉酶 Acid/$\alpha$-amylase | 噻虫啉 thiacloprid | [58] |
| 双响应 Dual response: pH/氧化还原 pH/Redox | 玉米醇溶蛋白 Zein | 碱性/谷胱甘肽 Alkaline/glutathione | 阿维菌素 abamectin | [59] |
| 双响应 Dual response: 氧化还原/酶 Redox/Enzyme | FeMOF | 谷胱甘肽/果胶酶 Glutathione/pectinase | 吡唑醚菌酯 pyraclostrobin | [60] |

### 1.1 pH 响应型纳米控释系统

pH 响应型纳米控释系统是基于载体材料中具有或被修饰酸性或碱性官能团，如酸性官能团有羧基、磺基等，碱性官能团有嘧啶、氨基等[35, 61]，分别在碱性或酸性条件下会发生溶胀、破裂等结构变化，缓慢释放农药活性成分[62-63]，从而达到控释效果的纳米载药系统。结合病原菌或害虫发生时的环境 pH 变化选择不同的官能团，构建随病虫害发生而释放的响应系统[64]。Ma 等[37] 根据立枯丝核菌 *Rhizoctonia solani* 在侵染时会释放草酸及纤维素酶的特点，通过将吡唑醚菌酯及羟甲基纤维素包封在 UIO-66 材料内，建立了一种 pH/酶双响应智能递送系统。生物测定结果表明，在防治番茄青枯病时，该系统的防治效果优于市售微胶囊剂，且对非靶标生物展现出良好的生物安全性。Gao 等[35] 将甲基丙烯酸缩水甘油酯 (glycidyl methacrylate, GMA) 和丙烯酸 (acrylic acid, AA) 两种富含羧基的碱性敏感分子的聚合物 P(GMAAA)，与中空介孔二氧化硅 (hollow mesoporous silica, HMS) 纳米载体结合，构建了一种介孔二氧化硅负载阿维菌素 (abamectin, Aba) 的 pH 响应纳米控释系统 Aba@HMS@P(GMA-AA)。该响应系统展现出优异的响应性及长效释放效果。其释放行为结果表明，在 pH 为 5 和 7 的条件下，阿维菌素 15 d 的累计释放量分别为 14% 和 13%， pH 为 10 时，阿维菌素 5 h 释放量为 39%，能够持续释放 15 d，其累计释放量为 87%，并且表现出对稻纵卷叶螟 *Cnaphalocrocis medinalis* 幼虫优异的防治效果，在 21 d 时，Aba@HMS@P(GMA-AA) 控释系统幼虫死亡率为对照组的两倍。Xu 等[65] 利用多巴胺在碱性条件下自发分解的特性，将其修饰于铜离子螯合的介孔二氧化硅载体上，通过负载嘧菌酯 (azoxystrobin，AZOX)，构建出具有 pH 响应的纳米控释系统。该系统对稻瘟病菌 *Pyricularia oryzae* 具有优异的防治效果，在 60 h 累积释放量达到 69%~88%。其生物活性试验结果表明，与嘧菌酯悬浮剂相比，控释系统对黄瓜白粉病具有更好的治疗效果。因此，利用 pH 敏感载体材料修饰的载药控释系统，不仅能智能响应环境条件释放农药活性成分，还表现出优异的防治效果[57, 66-67]。

### 1.2 光响应型纳米控释系统

光响应型纳米控释系统是利用光敏材料或在载体材料上修饰光刺激性结构[68]，在经过紫外光、可见光等不同波长的光刺激时，其光敏结构会发生裂解、异构、极性等变化，从而释放被包裹的农药活性成分[45] 的纳米载药系统。Gao 等[42] 构建了一种葫芦脲-百草枯-偶氮苯衍生物三元复合体的光响应型超分子囊泡，由于偶氮苯结构在紫外或阳光照射下会从反式异构体转换为顺式异构体，使得载药囊泡结构解离，从而具有控制释放作用。该超分子囊泡结构在黑暗条件下储存 210 d，展现出优异的稳定性。其释放动力学研究结果显示， 在自然光下，4 h 百草枯的累计释放率超过 80%，能够有效防治草害。体外毒性试验结果表明，其对人体肝脏细胞、斑马鱼、小鼠等表现出优异的生物安全性。Wang 等[43] 利用肉桂酸修饰二氧化硅纳米微球，构建一种新型光响应型二甲戊乐灵控释系统。在紫外或太阳光照射下，肉桂酸会发生异构，从而释放农药活性成分，72 h 累计释放量高于 80%，展现出良好的控释成效。与工业级二甲戊乐灵相比，除草效果更好、毒性更低。光响应型纳米载药控释系统不仅能够有效控制有害生物的发生，还能提供一种安全有效的防治策略，为发展环境友好型新制剂提供技术支持[46]。

### 1.3 温度响应型纳米控释系统

温度响应型纳米控释系统是利用温敏材料在特定温度下会刺激产生可逆响应，导致载体材料结构和性质发生变化，最终释放农药活性成分[47-48] 的纳米载药系统。对温敏性材料而言，当环境温度超过相变温度时，材料会从水溶液中分离、出现沉淀现象，进而实现农药活性成分的释放[69-70]。通常用于构建温度响应型纳米控释系统的温敏性聚合物材料有丙烯酰胺聚合物、羟丙基甲基纤维素、聚乙烯醇等[71]，将温敏材料的释放特性与田间病虫害发生规律相结合，能够实现农药的精准释放与智能防控。Shen 等[58] 根据田间虫害在高温时发生严重的规律，结合聚 *N*-异丙基丙烯酰胺 (poly *N*-isopropylacrylamide, PNIPAM) 的相变温度为 32 ℃ (与虫害发生规律吻合)，构建了一种 PNIPAM 基纳米凝胶负载高效氯氟氰菊酯的 Pickering 乳液，是一种温度依赖型纳米释放系统，其释放速率与温度变化呈正相关，与高温下害虫种群密度增长相匹配，在减少农药使用量 40% 的情况下，对菜青虫的防治效果依然优于市售高效氯氟氰菊酯悬浮剂的效果。Wan 等[53] 构建了一种基于聚 *N*-异丙基丙烯酰胺修饰 UIO-66 的

茚虫威温度响应型纳米控释系统，具有良好的负载能力及药物释放效果，其对茚虫威的负载率为78.69%，能够持续释放120 h，在15 ℃下释放量为26.58%，在40 ℃下，累计释放量为79%，即能够通过升高温度来获得更多的释放量。生物活性测定结果表明，其对草地贪夜蛾的防治效果优于茚虫威对照组。Gao等[51]将介孔二氧化硅作为缓释材料，利用温敏共聚物聚*N*-异丙基丙烯酰胺-甲基丙烯酸为载体外壳，建立了一种噻虫嗪温度响应型纳米缓释系统。该体系在低温时释放速率缓慢，释放量仅有25.03%；高温时释放迅速，释放量达50.39%，且高温条件下饲喂防治褐飞虱14 d的死亡率高达80%，显著高于对照组45%。温度响应型纳米控释系统更加适用于随田间温度变化而发生的严重的病虫害管理，可有效提高农药利用率，减少农药的投入量。

### 1.4 酶响应型纳米控释系统

酶在生物体生理生化反应和代谢过程中起着重要作用，具有高度特异性和选择性[52]，利用酶作为农药活性成分刺激释放的位点，能够实现更加精准、对靶的控释效果[55]。将酶响应控释技术应用于农业病虫害防治时，多种酶都能作为刺激因子，如病虫害侵染作物时作物释放的防御酶、植物病原菌产生的特异性酶、昆虫唾液及中肠的特异性酶等[72-74]。酶响应型纳米控释系统是利用载体材料负载农药并结合酶刺激因子构建的载药体系，在环境中响应特异性酶的变化，而迅速裂解、水解，释放农药活性成分，精准防治农业病虫害[75-76]。Liang等[32]以土壤中的脲酶作为响应因子，将异氰酸酯官能化的二氧化硅与聚乙烯亚胺通过脲键交联，构建了二甲戊乐灵脲酶响应系统。脲酶存在时，该系统30 h释放量高达81.94%，而非脲酶的环境中未检测到二甲戊乐灵的存在。与二甲戊乐灵乳油相比，该酶响应系统表现出更长的持效期，51 d的除草活性比乳油制剂高。Abdelrahman等[77]将咪鲜胺负载于经果胶修饰的介孔二氧化硅纳米粒子中，建立了一种可以响应病原物内部果胶酶刺激的控释系统，能够有效防治水稻稻瘟病。该纳米控释系统具有很好的控释效果，前3 d没有果胶酶时的释放量为12.48%，加入果胶酶后，至21 d，其累计释放量增加到74.55%。其杀菌活性试验结果表明，咪鲜胺纳米控释系统处理7 d和14 d的杀菌效果优于咪鲜胺乳油及原药。Gao等[78]利用羟丙基纤维素 (hydroxy propyl cellulose, HPC) 结合中空介孔二氧化硅纳米粒子 (HMS) 负载吡唑醚菌酯 (pyraclostrobine, PYR)，构建了一种基于pH/纤维素酶双响应纳米控释系统 (PYR-HMS-HPC)。该控释系统能够在酸性条件下通过纤维素酶水解和酯键的断裂释放农药活性成分。在pH值为3时，144 h的累计释放量为79.6%；在含纤维素酶和不含纤维素酶的溶液中，144 h的累计释放率分别为83.5%和15.5%。其抑菌试验结果表明，PYR-HMS-HPC在7~21 d的杀菌活性明显强于PYR原药。酶响应型纳米控释系统将病虫害相关酶作为响应因子，能够及时释放农药活性成分，有效提高农药利用率及防治效果。

## 2 叶面亲和型纳米农药载药系统

在利用植保器械进行叶面施药时，受作物叶面蜡质层、表面微纳结构、喷施速度、环境温湿度及风速等多种因素的影响，仅有极少部分药液能够沉积在作物叶片上并发挥控制病虫害的效果[79-80]。与此同时，药液的飞溅、漂移和流失会导致农药利用率极低[81-83]，农药活性成分流经土壤、河流，作用于非靶标生物，也会引发严重的环境污染及作物药害等问题[84-86]。因此，为了有效提高农药利用率，增强叶面施用药剂在作物表面的沉积和黏附显得尤为关键，这也是实现农业可持续发展和绿色发展的重要策略。

近年来，研究人员广泛关注农药在作物叶面的润湿及沉积行为。通过在药液中添加各种表面活性剂、蛋白聚集体、纳米低聚物颗粒、水凝胶等物质来提高药液在叶面上的滞留量[87-90]，其中纳米低聚物颗粒能够迅速在空气和液滴界面聚集，形成一层聚集体，从而有效降低药液的界面自由能和表面张力，有助于药液在叶面沉积、减少弹跳[91-92]。同时，当药液沉积在叶面时，形成的聚集体能与叶面微纳结构相互作用，使药液黏附于叶面上，避免雨水冲刷而导致的药液损失，提高农药在叶面上的持留量[93]。Zhao等[94]构建了一种邻苯二酚功能化帽状载体，利用其负载咪鲜胺和苯醚甲环唑，分别喷洒于小麦和水稻叶片上时，功能化载体通过拓扑效应驱动叶面上的微纳结构，可提高药液与叶片的亲和力，使其有效黏附于小麦和水稻叶片上，其滞留量相当于咪鲜胺乳油制剂在小麦上的140%，苯醚甲环唑乳油制剂在水稻

上的 187%，并且该载体还具有优异的缓释效果，能够持续释放药物 15 d，有效延长了农药持效期，在农药残留和抗冲性方面提高约 30%。Su 等[95] 利用牛血清白蛋白的淀粉样聚集体 (phase-transitioned bovine serum albumin, PTB) 来增强噻嗪酮在超疏水叶面的沉积，PTB 在作物叶片表面形成纳米膜，能够有效突破作物叶片超疏水结构，形成钉扎结构侵入叶面的微纳结构，有效提高噻嗪酮在叶面上的持留量，且在冲击力高于雨滴冲刷力 190 倍条件下模拟雨水冲刷叶面，噻嗪酮@PTB 组的保留量比噻嗪酮@水组高 6~11 倍。Cao 等[87] 利用戊醇调节吡唑醚菌酯微囊外壳的厚度与致密度，使其自发变形成“蜗牛吸盘”状结构，以提高其在叶面地黏附性及防治效果，经雨水冲刷后吡唑醚菌酯-戊醇微囊在黄瓜、花生和水稻叶片上的持留量分别达 62.81%、69.14% 和 75.50%，在田间防治花生叶斑病时，与对照组落叶率 90% 相比，吡唑醚菌酯-戊醇微囊的落叶率仅为 5%，植物最茂盛，表现出优异的防治效果。

针对作物叶面病虫害的威胁，过去的研究主要集中在叶片正面的喷施与防治。然而，作物叶片背面往往存在更难处理的问题，例如红蜘蛛、白粉虱的取食部位以及白锈病、霜霉病病原菌的侵染部位均为叶片的背面。在叶片背面喷施药物非常困难，不仅药液容易弹跳，而且由于重力作用会导致大量药液流失，造成农药浪费和环境污染。为解决这一难题，研究人员发现，利用自下而上的喷雾方式结合纳米材料的黏附功能，能够有效实现对叶片背面病虫害的控制[96]。Zhang 等[96] 以胆汁盐/阳离子表面活性剂凝聚体为甲维盐载体，能够实现药液在叶背面的有效沉积，当药液自下而上喷施在叶面上时，该凝聚体内部的网状结构在冲击过程中形成的钉扎结构能够有效附着在叶面上，防治药液回弹。在接触角为 155° 的超疏水作物番茄叶面喷施该药液，表现出高达 87.7% 的附着率，是使用传统助剂的 3~4 倍，能够有效保护番茄植株免受病虫害的威胁。

## 3 土壤用药纳米载药系统

土壤中的真菌、细菌、病毒及线虫会引起作物幼苗根部和茎部的腐烂，对农作物造成严重威胁[97]。目前，最常见的防治方式是土壤施药，然而农药在土壤中的分布受诸多因素限制，部分农药会被土壤表层的有机质吸附，部分农药受土壤理化性质及作物根系结构差异影响，造成农药在土壤中的迁移性差、分布有限、难以渗透至更深的土壤层，从而导致土壤制剂的防治效果不佳、利用率低等问题[98-100]。因此改良土壤施药技术、提高药物在土壤中的流动性成为防治土传病虫害的关键。

近年来，利用纳米技术改良土壤制剂在防治土传病虫害方面取得显著成效。纳米材料具有小尺寸、易迁移等特性，能够携带农药活性成分渗透至更深的土层，增加药物在土壤中的分布，从而提高防治效果[101]。Luo 等[102] 将吡唑醚菌酯封装于木质素改性的纳米胶囊中，用于提高其对镰刀菌 *Fusarium oxysporum* 的防治效果。结果表明，吡唑醚菌酯纳米胶囊在土壤中具有优异的移动性能，能均匀分布在番茄根际与菌丝表面，对番茄根腐病的防治效果是其纳米水乳剂的 5~6 倍，能够有效控制番茄根腐病的发生。后续 Jing 等[98] 利用囊壁材料苯基异氰酸酯修饰阿维菌素 B1a (abamectin B1a, AVB1a)，生成具有氨基甲酸酯结构的衍生物，该衍生物是一种农药活性结构，在土壤中具有良好的流动性，能够有效防治根结线虫的发生。土壤流动性试验结果表明，AVB1a 衍生物能够渗透至 20~25 cm 深的土层，而对照组只能在 0~5 cm 深处检测到，且 AVB 1a 衍生物能够破坏线虫的活力，降低线虫对植物根部的穿刺能力，从而保护作物健康。

土壤用药制剂的改良不仅可以利用纳米材料提高农药活性成分的移动性，还可以结合耕作方式，将农药添加至覆盖作物的薄膜中以控制病虫害的发生[103-104]，虽然这种方式对于土传病害的控制取得了一定的效果，但仍无法控制药物的作用时间且会受到环境因素的影响，导致其无法达到理想的作用效果。目前，缓释制剂与地膜结合的方法能有效解决这一局限，通过控制农药活性成分的释放，提高防治效果。Xie 等[105] 将吡唑醚菌酯微囊缓释剂与作物地膜相结合用于控制大豆根腐病的发生，其制备的温度响应型纳米微囊缓释剂在低温时缓慢释放，在高温时大豆根腐病发生严重的情况下迅速释放，从而有效控制大豆根腐病对种子的侵染，其种子发芽率接近 90%。

功能化纳米农药载药系统能够帮助农药在叶面、土壤等施药场景中充分发挥药效 (表 2)。适用

于叶面喷施的农药载药系统，其功能化材料往往具有水溶性好、流动性好、易于喷雾且对疏水/超疏水表面有强黏附性等优势，从而在喷施时能使药液有效沉积于作物叶面；土壤用药型纳米载药系统功能化材料的选择大多以分散性能为主，部分材料能够构建出负电性载药系统，从而增强其对土壤胶体的排斥力，更好地帮助农药活性成分在土壤中移动。因此，从作物环境的实际施药需求出发，构建功能化纳米载药系统可以进一步提升农药在作用过程中的性能，减少损失，在农业病虫害化学防治中有巨大的应用潜力。

**表 2 不同施药方式的功能化纳米农药载药系统**

**Table 2 Functional nanoparticle pesticide delivery systems with different application modes**

| 施药方式<br>Application method | 功能化材料<br>Functional material | 农药<br>Pesticide | 功能<br>Functionality | 参考文献<br>Reference |
|---|---|---|---|---|
| 叶面喷施<br>Foliage spray | 邻苯二酚<br>Catechol | 咪鲜胺/苯醚甲环唑<br>imidamine/phenacetoconazole | 叶面亲和<br>Foliar affinity<br>增加黏附性<br>Increase adhesion | [94] |
| | 牛血清白蛋白淀粉样聚集体<br>Phase-transitioned bovine serum albumin | 噻嗪酮<br>thiazinone | | [95] |
| | 戊醇<br>Pentanol | 吡唑醚菌酯<br>pyrazolesterin | | [87] |
| | 胆汁盐/阳离子表面活性剂凝聚体<br>Bile salts/cationic surfactant condensates | 甲氨基阿维菌素苯甲酸盐<br>emamectin | | [96] |
| | 海藻酸基纳米凝胶<br>Alginate based nanogels | 吡唑醚菌酯<br>pyrazolesterin | | [106] |
| | 单宁酸涂层纳米粒子<br>Tannin coated nanoparticles | 阿维菌素/嘧菌酯<br>abamectin/pyrimethil | | [107] |
| | 苯乙烯和甲基丙烯酸共聚物纳米颗粒<br>Styrene and methacrylate copolymer nanoparticles | 阿维菌素<br>abarmectin | | [108] |
| 土壤用药<br>Soil application | 木质素<br>Lignin | 吡唑醚菌酯<br>pyrazolesterin | 增加迁移性<br>Increase mobility | [102] |
| | 苯基异氰酸酯<br>Phenyl isocyanate | 阿维菌素<br>abamectin | | [98] |
| | 环氧树脂纳米胶囊<br>Epoxy nanocapsules | 阿维菌素<br>abamectin | | [109] |

## 4 纳米农药双载体系

过度使用农药会导致有害生物产生抗药性，增加防治难度，影响农产品质量安全。当推荐剂量无法控制害虫时，增加施药量可能导致农药残留超标，危及人类健康。因此，为缓解抗药性发展，需采用多种防治技术，提高农药利用率，实现农药减量增效。农药联合施用是一种有效的解决方法，其是将两种或两种以上的农药在田间混配在一起施用，它不仅能够避免单一药物的过度使用，还能有效提高农药利用率并扩大防治谱[110]，而且两种或多种作用机理不同的药物联合施用还能减轻选择压力，缓解有害生物产生抗药性[111-114]。

目前，一些学者将纳米材料的缓释作用与农药联合施用策略相结合，构建纳米农药双载体系，如纳米囊农药双载体系 (图 2)，即在单个纳米载体中负载两种农药活性成分，一次施药后能同时发挥两种药物的药效从而减少农药用量和环境污染。如 Cui 等[115] 首次开发的井岗霉素和噻呋酰胺的纳米双载缓释系统，表现出良好的叶面铺展性与防治效果，该纳米双载缓释系统对水稻纹枯病的防治效果是两种农药联合使用的 4.2 倍。Suraphan 等[116] 建立了一种阿维菌素和氯虫苯甲酰胺的多孔

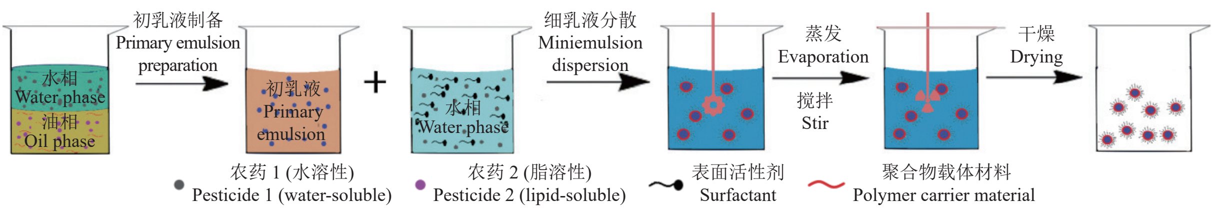


**图 2 纳米囊农药双载体系的制备工艺**

**Fig. 2 Preparation process of double-loaded pesticide system in nanocapsules**

聚乳酸双载体系，包封率高达 88%，能够持续释放 168 h，累计释放量 98.4%。生物活性试验结果表明，该双载体系对小菜蛾的防治效果远高于氯虫苯甲酰胺和阿维菌素的单一制剂，有效提高药效，减少了农药施用量。An 等[117] 以聚乳酸为载体，构建了一种阿维菌素与呋虫胺的纳米双载体系。田间试验结果表明，该体系对梨小食心虫有着优异的防治效果，其施药两次与分别施用两种农药 3 次的效果相当，害虫抑制率均高于 80%，农药使用总量减少 33%。近期 Wang 等[118] 构建了一种基于树状介孔二氧化硅为载体的氯虫苯甲酰胺与多杀菌素的双载纳米体系，该体系具有谷胱甘肽/pH 双重刺激响应，能够智能释放药物，144 h 时在 pH 值和谷胱甘肽的双重作用下，氯虫苯甲酰胺与多杀菌素的累积释放量分别为 94.53% 和 57.05%。虽然目前针对纳米农药双载体系的研究才刚开始，但采取农药协同策略是实现农药减量增效、实现绿色农业的有效途径。

## 5 总结与展望

功能化纳米农药载药系统有着诸多优势[119]，可以通过智能响应控释、叶面亲和修饰、组分协同增效等不同方式，实现农药的减量增效与功能提升。纳米农药智能响应控释系统能够特异性响应病虫害发生的环境因子，针对病虫害发生的趋势与变化调控药物的释放特性，提高药物对病虫害靶向递送的效率，增强化学防治的智能性和精准性，减少农药用量。叶面亲和型纳米载药系统可针对疏水性的作物叶面的结构特征，利用载药系统的特性增加药液在叶面的黏附，促进药液的沉积，有效改善叶面喷施制剂药液飞溅和流失等问题。同时，由于纳米载药系统的精细粒径与良好的分散性，可以在土壤用药的施药环境下有效改善农药在土壤中的流动性，使农药活性成分深入土层，增加与根系的接触面积，更好地控制根系病虫害的发生。利用纳米材料与技术负载两种不同的农药有效成分，构建纳米农药双载体系在延长农药的持效期、实现农药的协同增效和减少喷药次数与剂量方面也显示了良好的效果，在缓解有害生物抗药性方面也具有潜在的应用前景。因此，功能化纳米农药载药系统的发展为实现农药精准高效施药，推动农药释放模式不断向智能化、可调控与协同化的方向发展。

功能化纳米农药载药系统给农业病虫害防治带来了新机遇，有望成为可持续农业发展的有效工具。目前纳米农药载药系统的构建与表征等研究不断丰富，纳米农药剂型创制逐步走向产业化，针对众多不同载体材料与载药结构的纳米农药载药系统，建立可量产化的制备工艺与经济便捷的载药体系仍需进一步进行研究，开发低成本与安全环保的载体材料是实现功能化纳米农药载药系统量产化的重要基础。其次，功能化纳米农药载药系统的评价方法与使用标准需要进一步完善，以便为纳米农药新制剂的大面积推广奠定基础。功能化纳米农药载药系统已经成为农药制剂领域的研究热点，在众多科研工作者的不断创新下，功能化纳米农药载药系统的构建与评价方法将会进一步完善，纳米农药新制剂的产业化有望为推进农业绿色与可持续发展做出重要贡献。

## 参考文献 (References):


[ 1 ] FEYNMAN R P. There's plenty of room at the bottom[J]. Resonance, 2011, 16(9): 890-905.

[ 2 ] POKROPIVNY V V, SKOROKHOD V V. Classification of nanostructures by dimensionality and concept of surface forms engineering in nanomaterial science[J]. Mater Sci Eng C, 2007, 27(5-8): 990-993.

[ 3 ] BAYDA S, ADEEL M, TUCCINARDI T, et al. The history of nanoscience and nanotechnology: from chemical-physical applications to nanomedicine[J]. Molecules, 2019, 25(1): 112.

[ 4 ] 孙长娇, 崔海信, 王琰, 等. 纳米材料与技术在农业上的应用研究进展[J]. 中国农业科技导报, 2016, 18(1): 18-25.
SUN C J, CUI H X, WANG Y, et al. Studies on applications of nanomaterial and nanotechnology in agriculture[J]. J Agric Sci Technol, 2016, 18(1): 18-25.

[ 5 ] YAN S, REN B Y, SHEN J. Nanoparticle-mediated double-stranded RNA delivery system: a promising approach for sustainable pest management[J]. Insect Sci, 2021, 28(1): 21-34.

[ 6 ] QIAO L L, NIÑO-SÁNCHEZ J, HAMBY R, et al. Artificial nanovesicles for dsRNA delivery in spray induced gene silencing for crop protection[J]. BioRxiv, 2023, 21(4): 854-865.

[ 7 ] YAN S, QIAN J, CAI C, et al. Spray method application of transdermal dsRNA delivery system for efficient gene silencing and pest control on soybean aphid *Aphis glycines*[J]. J Pest Sci, 2020, 93(1): 449-459.

[ 8 ] ATHANASSIOU C G, KAVALLIERATOS N G, BENELLI G, et al. Nanoparticles for pest control: current status and future perspectives[J]. J Pest Sci, 2018, 91(1): 1-15.

[ 9 ] GOGOS A, KNAUER K, BUCHELI T D. Nanomaterials in plant protection and fertilization: current state, foreseen applications, and research priorities[J]. J Agric Food Chem, 2012, 60(39): 9781-9792.

[ 10 ] HUANG B N, CHEN F F, SHEN Y, et al. Advances in targeted pesticides with environmentally responsive controlled release by nanotechnology[J]. Nanomaterials, 2018, 8(2): 102.

[ 11 ] NAIR R, VARGHESE S H, NAIR B G, et al. Nanoparticulate material delivery to plants[J]. Plant Sci, 2010, 179(3): 154-163.

[ 12 ] ZHAO X, CUI H X, WANG Y, et al. Development strategies and prospects of nano-based smart pesticide formulation[J]. J Agric Food Chem, 2018, 66(26): 6504-6512.

[ 13 ] 李晶, 郭亮, 崔海信, 等. 纳米农药在植物中的吸收转运研究进展[J]. 植物学报, 2020, 55(4): 513-528.
LI J, GUO L, CUI H X, et al. Research progress on uptake and transport of nanopesticides in plants[J]. Chin Bull Bot, 2020, 55(4): 513-528.

[ 14 ] GHORMADE V, DESHPANDE M V, PAKNIKAR K M. Perspectives for nano-biotechnology enabled protection and nutrition of plants[J]. Biotechnol Adv, 2011, 29(6): 792-803.

[ 15 ] ZHAO X, CUI H X, CHEN W J, et al. Morphology, structure and function characterization of PEI modified magnetic nanoparticles gene delivery system[J]. Plos One, 2014, 9(6): e98919.

[ 16 ] MITTER N, WORRALL E A, ROBINSON K E, et al. Clay nanosheets for topical delivery of RNAi for sustained protection against plant viruses[J]. Nat Plants, 2017, 3: 16207.

[ 17 ] ZHANG X, ZHANG J, ZHU K Y. Chitosan/double-stranded RNA nanoparticle-mediated RNA interference to silence chitin synthase genes through larval feeding in the African malaria mosquito (*Anopheles gambiae*)[J]. Insect Mol Biol, 2010, 19(5): 683-693.

[ 18 ] WANG Z W, LI Y, ZHANG B R, et al. Functionalized carbon dot-delivered RNA nano fungicides as superior tools to control *Phytophthora* pathogens through plant RdRP1 mediated spray-induced gene silencing[J]. Adv Funct Mater, 2023, 33(22): 2213143.

[ 19 ] JIA X, SHENG W B, LI W, et al. Adhesive polydopamine coated avermectin microcapsules for prolonging foliar pesticide retention[J]. ACS Appl Mater Interfaces, 2014, 6(22): 19552-19558.

[ 20 ] KHOT L R, SANKARAN S, MAJA J M, et al. Applications of nanomaterials in agricultural production and crop protection: a review[J]. Crop Prot, 2012, 35: 64-70.

[ 21 ] ZHANG Z, YANG N, YU J, et al. Research progress of a pesticide polymer-controlled release system based on polysaccharides[J]. Polymers, 2023, 15(13): 2810.

[ 22 ] PÉREZ-DE-LUQUE A, RUBIALES D. Nanotechnology for parasitic plant control[J]. Pest Manag Sci, 2009, 65(5): 540-545.

[ 23 ] 周艺峰, 武锦, 陈静, 等. APEP 型乳化剂在农药纳米胶囊制备中的应用研究[J]. 安徽大学学报 (自然科学版), 2007, 31(3): 65-68.
ZHOU Y F, WU J, CHEN J, et al. Applied research of APEP-type polymerizable emulsifier in the preparation of pesticide nanocapsule[J]. J Anhui Univ (Nat Sci Ed), 2007, 31(3): 65-68.

[ 24 ] WANG Y, WANG A Q, WANG C X, et al. Synthesis and characterization of emamectin-benzoate slow-release microspheres with different surfactants[J]. Sci Rep, 2017, 7(1): 12761.

[ 25 ] WANG Q, SHEN M F, LI W J, et al. Controlled-release of fluazinam from biodegradable PLGA-based microspheres[J]. J Environ Sci Health Part B, 2019, 54(10): 810-816.

[ 26 ] FU Z N, CHEN K, LI L, et al. Spherical and spindle-like abamectin-loaded nanoparticles by flash nanoprecipitation for southern root-knot nematode control: preparation and characterization[J]. Nanomaterials, 2018, 8(6): 449.

[ 27 ] 郭艳珍. 基于界面聚合法的乙草胺微胶囊研制及其释放机理研究[D]. 重庆: 西南大学, 2014.
GUO Y Z. Study on the preparation and the release mechanism of acetochlor microcapsules produced by interfacial polymerization method[D]. Chongqing: Southwest University, 2014.

[ 28 ] 宋倩, 梅向东, 黄啟良, 等. 乳液聚合法制备阿维菌素微胶囊及其生物活性研究[J]. 农药学学报, 2009, 11(3): 392-394.
SONG Q, MEI X D, HUANG Q L, et al. Preparation of abamectin microcapsules by means of emulsion polymerization and it's bioactivity[J]. Chin J Pestic Sci, 2009, 11(3): 392-394.

[ 29 ] VILLAVERDE J J, SEVILLA-MORÁN B, LÓPEZ-GOTI C, et al. An overview of nanopesticides in the framework of European legislation[M]//New pesticides and soil sensors. United States: Elsevier Science & Technology, 2017: 227-271.

[ 30 ] 孙长娇, 王琰, 赵翔, 等. 纳米农药剂型与其减施增效机理研究进展[J]. 农药学学报, 2020, 22(2): 205-213.
SUN C J, WANG Y, ZHAO X, et al. Progress on categories and synergistic mechanism of nanopesticides[J]. Chin J Pestic Sci, 2020, 22(2): 205-213.

[ 31 ] GUO M C, ZHANG W B, DING G L, et al. Preparation and characterization of enzyme-responsive emamectin benzoate microcapsules based on a copolymer matrix of silica-epichlorohydrin-carboxymethylcellulose[J]. RSC Adv, 2015, 5(113): 93170-93179.

[ 32 ] LIANG Y, GUO M C, FAN C, et al. Development of novel urease-responsive pendimethalin microcapsules using silica-IPTS-PEI as controlled release carrier materials[J]. ACS Sustain Chem Eng, 2017, 5(6): 4802-4810.

[ 33 ] LI N J, SUN C J, JIANG J J, et al. Advances in controlled-release pesticide formulations with improved efficacy and targetability[J]. J Agric Food Chem, 2021, 69(43): 12579-12597.

[ 34 ] CAMARA M C, CAMPOS E V R, MONTEIRO R A, et al. Development of stimuli-responsive nano-based pesticides: emerging opportunities for agriculture[J]. J Nanobiotechnol, 2019, 17(1): 100.

[ 35 ] GAO Y H, ZHANG Y H, HE S, et al. Fabrication of a hollow mesoporous silica hybrid to improve the targeting of a pesticide[J]. Chem Eng J, 2019, 364: 361-369.

[ 36 ] LIANG W L, CHENG J L, ZHANG J D, et al. pH-Responsive on-demand alkaloids release from core-shell ZnO@ZIF-8 nanosphere for synergistic control of bacterial wilt disease[J]. ACS Nano, 2022, 16(2): 2762-2773.

[ 37 ] MA Y J, YU M, WANG Y M, et al. A pH/cellulase dual stimuli-responsive cellulose-coated metal-organic framework for eco-friendly fungicide delivery[J]. Chem Eng J, 2023, 462: 142190.

[ 38 ] MA Y J, WANG Y M, ZHAO R, et al. pH-Responsive ZIF-8 film-coated mesoporous silica nanoparticles for clean, targeted delivery of fungicide and environmental hazard reduction[J]. J Environ Chem Eng, 2023, 11(6): 111513.

[ 39 ] KAN Q H, LU K, DENG R Q, et al. An alkali-triggered polydopamine modified mesoporous silica nanopesticide for smart delivery of chlorpyrifos with low loss[J]. Acs Agric Sci Technol, 2022, 2(3): 501-511.

[ 40 ] PAN H, HUANG W L, WU L T, et al. A pH dual-responsive multifunctional nanoparticle based on mesoporous silica with metal-polymethacrylic acid gatekeeper for improving plant protection and nutrition[J]. Nanomaterials, 2022, 12(4): 687.

[ 41 ] XIAO D X, CHENG J L, LIANG W L, et al. Metal-phenolic coated and prochloraz-loaded calcium carbonate carriers with pH responsiveness for environmentally-safe fungicide delivery[J]. Chem Eng J, 2021, 418: 129274.

[ 42 ] GAO C, HUANG Q X, LAN Q P, et al. A user-friendly herbicide derived from photo-responsive supramolecular vesicles[J]. Nat Commun, 2018, 9(1): 2967.

[ 43 ] WANG M Y, LOU J Y, CHEN Y P, et al. Preparation and properties of photoresponsive pendimethalin@silica-cinnamamide/γ-CD microspheres for pesticide controlled release[J]. J Agric Food Chem, 2023, 71(5): 2270-2278.

[ 44 ] CHEN C W, ZHANG G L, DAI Z Y, et al. Fabrication of light-responsively controlled-release herbicide using a nanocomposite[J]. Chem Eng J, 2018, 349: 101-110.

[ 45 ] BERTRAND O, GOHY J F. Photo-responsive polymers: synthesis and applications[J]. Polym Chem, 2017, 8(1): 52-73.

[ 46 ] ATTA S, BERA M, CHATTOPADHYAY T, et al. Nano-pesticide formulation based on fluorescent organic photoresponsive nanoparticles: for controlled release of 2,4-D and real time monitoring of morphological changes induced by 2,4-D in plant systems[J]. RSC Adv, 2015, 5(106): 86990-86996.

[ 47 ] SCHMALJOHANN D. Thermo- and pH-responsive polymers in drug delivery[J]. Adv Drug Deliv Rev, 2006, 58(15): 1655-1670.

[ 48 ] RON E S, BROMBERG L E. Temperature-responsive gels and thermogelling polymer matrices for protein and peptide delivery[J]. Adv Drug Deliv Rev, 1998, 31(3): 197-221.

[ 49 ] DU Q, DING X Q, GAO F, et al. Thermo-responsive liposome nano-vesicles for co-delivery of emamectin benzoate and nitenpyram with synergistic pest control[J]. Chem Eng J, 2024, 479: 147548.

[ 50 ] LIU Y A, HUANG Y Q, LIU J W, LIU J. A temperature-responsive selenium nanohydrogel for strawberry grey mould management[J]. J Mater Chem B, 2022, 10(27): 5231-5241.

[ 51 ] GAO Y H, XIAO Y N, MAO K K, et al. Thermoresponsive polymer-encapsulated hollow mesoporous silica nanoparticles and their application in insecticide delivery[J]. Chem Eng J, 2020, 383: 123169.

[ 52 ] HU Q Y, KATTI P S, GU Z. Enzyme-responsive nanomaterials for controlled drug delivery[J]. Nanoscale, 2014, 6(21): 12273-12286.

[ 53 ] WAN M H, SONG S J, FENG W L, et al. Metal-organic framework (UiO-66)-based temperature-responsive pesticide delivery system for controlled release and enhanced insecticidal performance against *Spodoptera frugiperda*[J]. ACS Appl Bio Mater, 2022, 5(8): 4020-4027.

[ 54 ] KAZIEM A E, YANG L P, LIN Y G, et al. Pest invasion-responsive hollow mesoporous silica-linked carboxymethyl starch nanoparticles for smart abamectin delivery[J]. ACS Appl Nano Mater, 2022, 5(3): 3458-3469.

[ 55 ] ZELZER M, ULIJN R V. Enzyme-responsive polymers: properties, synthesis and applications[M]//Smart polymers and their applications. Amsterdam: Elsevier, 2014: 166-203.

[ 56 ] YANG L P, KAZIEM A E, LIN Y G, et al. Carboxylated β-cyclodextrin anchored hollow mesoporous silica enhances insecticidal activity and reduces the toxicity of indoxacarb[J]. Carbohyd Polym, 2021, 266: 118150.

[ 57 ] XIANG Y, ZHANG G, CHI Y, et al. Fabrication of a controllable nanopesticide system with magnetic collectability[J]. Chem Eng J, 2017, 328: 320-330.

[ 58 ] SHEN Y, AN C C, JIANG J J, et al. Temperature-dependent nanogel for pesticide smart delivery with improved foliar dispersion and bioactivity for efficient control of multiple pests[J]. ACS Nano, 2022, 16(12): 20622-20632.

[ 59 ] ZHAO M, LI P Q, ZHOU H J, et al. pH/redox dual responsive from natural polymer-based nanoparticles for on-demand delivery of pesticides[J]. Chem Eng J, 2022, 435: 134861.

[ 60 ] LIANG Y, WANG S J, JIA H J, et al. Pectin functionalized metal-organic frameworks as dual-stimuli-responsive carriers to improve the pesticide targeting and reduce environmental risks[J]. Colloid surface B, 2022, 219: 112796.

[ 61 ] TAO W, WANG J Q, PARAK W J, et al. Nanobuffering of pH-responsive polymers: a known but sometimes overlooked phenomenon and its biological applications[J]. ACS Nano, 2019, 13(5): 4876-4882.

[ 62 ] KOCAK G, TUNCER C, BÜTÜN V. pH-Responsive polymers[J]. Polym Chem, 2017, 8(1): 144-176.

[ 63 ] BAE Y, FUKUSHIMA S, HARADA A, et al. Design of environment-sensitive supramolecular assemblies for intracellular drug delivery: polymeric micelles that are responsive to intracellular pH change[J]. Angew Chem Int Ed Engl, 2003, 42(38): 4640-4643.

[ 64 ] CHOUDHARY R C, KUMARASWAMY R V, KUMARI S, et al. Cu-chitosan nanoparticle boost defense responses and plant growth in maize (*Zea mays* L.)[J]. Sci Rep, 2017, 7(1): 9754.

[ 65 ] XU C L, SHAN Y P, BILAL M, et al. Copper ions chelated mesoporous silica nanoparticles via dopamine chemistry for controlled pesticide release regulated by coordination bonding[J]. Chem Eng J, 2020, 395: 125093.

[ 66 ] CHEN M S, JENSEN S P, HILL M R, et al. Synthesis of amphiphilic polysuccinimide star copolymers for responsive delivery in plants[J]. Chem Commun, 2015, 51(47): 9694-9697.

[ 67 ] WEN H J, ZHOU H J, HAO L, et al. Enzyme cum pH dual-responsive controlled release of avermectin from functional polydopamine microcapsules[J]. Colloids Surf B Biointerfaces, 2020, 186: 110699.

[ 68 ] ESSER-KAHN A P, ODOM S A, SOTTOS N R, et al. Triggered release from polymer capsules[J]. Macromolecules, 2011, 44(14): 5539-5553.

[ 69 ] ZHANG Q L, WEBER C, SCHUBERT U S, et al. Thermoresponsive polymers with lower critical solution temperature: from fundamental aspects and measuring techniques to recommended turbidimetry conditions[J]. Mater Horiz, 2017, 4(2): 109-116.

[ 70 ] KIM Y J, MATSUNAGA Y T. Thermo-responsive polymers and their application as smart biomaterials[J]. J Mater Chem B, 2017, 5(23): 4307-4321.

[ 71 ] GANTA S, DEVALAPALLY H, SHAHIWALA A, et al. A review of stimuli-responsive nanocarriers for drug and gene delivery[J]. J Control Release, 2008, 126(3): 187-204.

[ 72 ] AKBAR S M, SHARMA H C. Alkaline serine proteases from *Helicoverpa armigera*: potential candidates for industrial applications[J]. Arch Insect Biochem Physiol, 2017, 94(1): 10.1002/arch. 21367.

[ 73 ] TABATABAEI P R, HOSSEININAVEH V, GOLDANSAZ S H, TALEBI K. Biochemical characterization of digestive proteases and carbohydrases of the carob moth, *Ectomyelois ceratoniae* (Zeller) (Lepidoptera: Pyralidae)[J]. J Asia-Pac Entomol, 2011, 14(2): 187-194.

[ 74 ] KAZIEM A E, GAO Y H, ZHANG Y, et al. α-Amylase triggered carriers based on cyclodextrin anchored hollow mesoporous silica for enhancing insecticidal activity of avermectin against *Plutella xylostella*[J]. J Hazard Mater, 2018, 359: 213-221.

[ 75 ] FAN C, GUO M C, LIANG Y, et al. Pectin-conjugated silica microcapsules as dual-responsive carriers for increasing the stability and antimicrobial efficacy of kasugamycin[J]. Carbohydr Polym,

2017, 172: 322-331.

[76] ZHANG X Q, HE Y, YUAN Z T, et al. A pH- and enzymatic-responsive nanopesticide to control pea aphids and reduce toxicity for earthworms[J]. Sci Total Environ, 2023, 861: 160610.

[77] ABDELRAHMAN T M, QIN X Y, LI D L, et al. Pectinase-responsive carriers based on mesoporous silica nanoparticles for improving the translocation and fungicidal activity of prochloraz in rice plants[J]. Chem Eng J, 2021, 404: 126440.

[78] GAO Y H, LIU Y, QIN X Y, et al. Dual stimuli-responsive fungicide carrier based on hollow mesoporous silica/hydroxypropyl cellulose hybrid nanoparticles[J]. J Hazard Mater, 2021, 414: 125513.

[79] KOCH K, BHUSHAN B, BARTHLOTT W. Diversity of structure, morphology and wetting of plant surfaces[J]. Soft Matter, 2008, 4(10): 1943-1963.

[80] KOCH K, BHUSHAN B, BARTHLOTT W. Multifunctional surface structures of plants: an inspiration for biomimetics[J]. Prog Mater Sci, 2009, 54(2): 137-178.

[81] MATTOS B D, GRECA L G, TARDY B L, et al. Green formation of robust supraparticles for cargo protection and hazards control in natural environments[J]. Small, 2018: e1801256.

[82] XIANG Y B, WANG M, SUN X, et al. Controlling pesticide loss through nanonetworks[J]. ACS Sustain Chem Eng, 2014, 2(4): 918-924.

[83] ANDRADE V S, GUTIERREZ M F, REGALDO L, et al. Influence of rainfall and seasonal crop practices on nutrient and pesticide runoff from soybean dominated agricultural areas in Pampean streams, Argentina[J]. Sci Total Environ, 2021, 788: 147676.

[84] ATASHGAHI S, SÁNCHEZ-ANDREA I, HEIPIEPER H J, et al. Prospects for harnessing biocide resistance for bioremediation and detoxification[J]. Science, 2018, 360(6390): 743-746.

[85] AN X F, WU Z S, SHI W, et al. Biochar for simultaneously enhancing the slow-release performance of fertilizers and minimizing the pollution of pesticides[J]. J Hazard Mater, 2021, 407: 124865.

[86] SINGH A, DHIMAN N, KAR A K, et al. Advances in controlled release pesticide formulations: prospects to safer integrated pest management and sustainable agriculture[J]. J Hazard Mater, 2020, 385: 121525.

[87] CAO H C, CHEN Y, QIAN Z G, et al. Amphiphilicity-driven small alcohols regulate the flexibility of pesticide-loaded microcapsules for better foliar adhesion and utilization[J]. ACS Appl Mater Interfaces, 2023, 15(17): 21444-21456.

[88] SONG M R, JU J, LUO S Q, et al. Controlling liquid splash on superhydrophobic surfaces by a vesicle surfactant[J]. Sci Adv, 2017, 3(3): e1602188.

[89] BAO Z P, WU Y L, SONG R D, et al. The simple strategy to improve pesticide bioavailability and minimize environmental risk by effective and ecofriendly surfactants[J]. Sci Total Environ, 2022, 851(Pt 1): 158169.

[90] BAO Z P, ZENG A J, GAO T, et al. Controlling impact behavior on superhydrophobic surfaces for droplets of nonionic surfactants by tailoring hydrophilic chain length[J]. J Mol Liq, 2022, 346: 117071.

[91] LUO S Q, CHEN Z D, DONG Z C, et al. Uniform spread of high-speed drops on superhydrophobic surface by live-oligomeric surfactant jamming[J]. Adv Mater, 2019, 31(41): e1904475.

[92] LI Z L, LI Z H, GAO Y X, et al. Assemblies disaggregation and diffusion dictated droplet impact and wetting behaviors on hydrophobic surface[J]. J Mol Liq, 2021, 339: 116826.

[93] AN C C, SUN C J, LI N J, et al. Nanomaterials and nanotechnology for the delivery of agrochemicals: strategies towards sustainable agriculture[J]. J Nanobiotechnology, 2022, 20(1): 11.

[94] ZHAO K F, WANG B, ZHANG C H, et al. Catechol functionalized hat-shape carriers for prolonging pesticide retention and flush resistance on foliage[J]. Chem Eng J, 2021, 420: 127689.

[95] SU H, LIU Y C, GAO Y T, et al. Amyloid-like protein aggregation toward pesticide reduction[J]. Adv Sci, 2022, 9(13): e2105106.

[96] ZHANG L C, WANG J, FAN Y X, et al. Coacervate-enhanced deposition of sprayed pesticide on hydrophobic/superhydrophobic abaxial leaf surfaces[J]. Adv Sci, 2023, 10(18): e2300270.

[97] 曹坳程, 张大琪, 方文生, 等. 土传病害防治技术进展及面临的挑战[J]. 植物保护, 2023, 49(5): 260-269.
CAO A C, ZHANG D Q, FANG W S, et al. Progresses and challenges in soil-borne disease prevention and control technology[J]. Plant Prot, 2023, 49(5): 260-269.

[98] JING T F, ZHANG D X, PAN S H, et al. Phenyl isocyanate-modified avermectin B1a improves the efficacy against plant-parasitic nematode diseases by facilitating its soil mobility[J]. ACS Sustain Chem Eng, 2020, 8(5): 2310-2319.

[99] RAZA W, LING N, ZHANG R F, et al. Success evaluation of the biological control of *Fusarium* wilts of cucumber, banana, and tomato since 2000 and future research strategies[J]. Crit Rev Biotechnol, 2017, 37(2): 202-212.

[100] PENG H, JIAN J Z, LONG H B, et al. Self-assembled nanonematicide induces adverse effects on oxidative stress, succinate dehydrogenase activity, and ATP generation[J]. ACS Appl Mater Interfaces, 2023, 15(26): 31173-31184.

[101] JING T F, ZHANG D X, ZHANG Y Z, et al. Adsorption behaviour and mechanism of avermectin-based pesticides in soil driven by H-bonds formed between the compounds and humus[J]. Chem Eng J, 2023, 459: 141647.

[102] LUO J, ZHANG D X, JING T, et al. Pyraclostrobin loaded lignin-modified nanocapsules: delivery efficiency enhancement in soil improved control efficacy on tomato *Fusarium* crown and root rot[J]. Chem Eng J, 2020, 394: 124854.

[103] CHEN G, CAO L D, CAO C, et al. Effective and sustained control of soil-borne plant diseases by biodegradable polyhydroxybutyrate mulch films embedded with fungicide of prothioconazole[J]. Molecules, 2021, 26(3): 762.

[104] LIANG W L, ZHAO Y, XIAO D X, et al. A biodegradable water-triggered chitosan/hydroxypropyl methylcellulose pesticide mulch film for sustained control of *Phytophthora sojae* in soybean (*Glycine max* L. Merr.)[J]. J Clean Prod, 2020, 245: 118943.

[105] XIE Z G, XIONG Q Y, FANG Y, et al. Novel biodegradable composite mulch film embedded with temperature-responsive pesticide microcapsules for durable control of *Phytophthora* root rot on soybean[J]. ACS Sustain Chem Eng, 2023, 11(26): 9868-9879.

[106] MAI K Y, YANG S J, ZHAO X Y, et al. Multi-bioinspired alginate-based gel coatings formed by dynamic metal-ligand assembly for enhancing foliar affinity and rain-fastness of pesticides[J]. Chem Eng J, 2024, 479: 147357.

[107] YU M L, SUN C J, XUE Y M, et al. Tannic acid-based nanopesticides coating with highly improved foliage adhesion to enhance foliar retention[J]. Rsc Adv, 2019, 9(46): 27096-27104.

[108] LIANG J, YU M L, GUO L Y, et al. Bioinspired development of P(st-MAA)-avermectin nanoparticles with high affinity for foliage to

enhance folia retention[J]. J Agric Food Chem, 2018, 66(26): 6578-6584.
[109] DU J, WANG C L, LIU Y K, et al. One-pot construction of epoxy resin nanocarrier delivering abamectin and its efficacy on plant root-knot nematodes[J]. Pest Manag Sci, 2023, 79(9): 3103-3113.
[110] SHI X G, QIAO K, LI B T, ZHANG S A. Integrated management of *Meloidogyne incognita* and *Fusarium oxysporum* in cucumber by combined application of abamectin and fludioxonil[J]. Crop Prot, 2019, 126: 104922.
[111] HERNÁNDEZ A F, GIL F, LACASAÑA M. Toxicological interactions of pesticide mixtures: an update[J]. Arch Toxicol, 2017, 91(10): 3211-3223.
[112] ST CLAIR C R, NORRIS E J, MASLOSKI K E, et al. Evaluation of pyrethroids and organophosphates in insecticide mixtures for management of western corn rootworm larvae[J]. Pest Manag Sci, 2020, 76(11): 3871-3878.
[113] AHMED K, FREED S, SHOUKAT R F, et al. Efficacy of entomopathogenic fungi with insecticides mixtures against *Oxycarenus hyalinipennis* (Costa) (Lygaeidae: Hemiptera)[J]. Pak J Zool, 2020, 52(2): 573.
[114] ROY D, BISWAS S, BISWAS A, et al. Can insecticide mixtures be considered to surmount neonicotinoid resistance in *Bemisia tabaci*?[J]. J Asia Pac Entomol, 2022, 25(2): 101901.
[115] CUI J X, SUN C J, WANG A Q, et al. Dual-functionalized pesticide nanocapsule delivery system with improved spreading behavior and enhanced bioactivity[J]. Nanomaterials, 2020, 10(2): 220.
[116] SURAPHAN N, FAN L F, LIU B X, et al. Co-delivery of chlorantraniliprole and avermectin with a polylactide microcapsule formulation[J]. RSC Adv, 2020, 10(43): 25418-25425.
[117] AN C C, CUI J X, YU Q, et al. Polylactic acid nanoparticles for co-delivery of dinotefuran and avermectin against pear tree pests with improved effective period and enhanced bioactivity[J]. Int J Biol Macromol, 2022, 206: 633-641.
[118] WANG K, WANG Y, WU Y Y, et al. A novel dual stimuli-responsive and double-loaded insecticidal nanoformulation for efficient control of insect pest[J]. Chem Eng J, 2023, 474: 146012.
[119] USMAN M, FAROOQ M, WAKEEL A, et al. Nanotechnology in agriculture: current status, challenges and future opportunities[J]. Sci Total Environ, 2020, 721: 137778.

(责任编辑: 金淑惠)

• 本期封面文章 •

## 生防芽孢杆菌种子处理剂 WS20 的研制及对甘蓝枯萎病的防治效果


芽孢杆菌类微生物制剂能有效控制植物病害。本研究在明确生防菌萎缩芽孢杆菌ZY1825 菌株对甘蓝枯萎病菌的拮抗抑菌效果及生防菌最佳发酵条件的基础上，以ZY1825 菌株发酵液为种子处理剂活性成分，筛选确定了分散剂、成膜剂、稳定剂及防冻剂等助剂组合的最佳质量分数为：木质素磺酸钠 4%、羧甲基纤维素 0.25%、膨润土 1%、乙二醇 0.5%，将 ZY1825 菌株发酵液 ($9.28 \times 10^9$ cfu/mL) 与混合助剂按体积比 2 : 1 均质混合，制得生防芽孢杆菌种子处理剂 WS20，经测试其成膜时间为 1.45 min，包衣均匀度93.06%，货架期可达 150 d，热贮和低温稳定性等指标均符合种子处理悬浮剂及微生物制剂的国家相关标准。采用 WS20 种子处理剂按药种质量比 1 : 30 包衣甘蓝种子，对甘蓝枯萎病的盆栽防效为 64.94%。研究结果可为利用芽孢杆菌制备种子处理剂以及土传性病害的生物防治提供参考。

*Bacillus*-based microbial agents can effectively control plant diseases. In this study, the antagonistic and inhibitory effects of *B. atrophicus* ZY1825 on *Fusarium* wilt of cabbage and the optimal fermentation conditions were revealed. Moreover, using ZY1825 as the active ingredient of the seed treatment agent, the optimum mass fractions of the dispersant, film-forming agent, stabilizer, and anti-freezing agent were selected as sodium lignosulfonate 4%, carboxymethyl cellulose 0.25%, bentonite 1%, and ethylene glycol 0.5%. The biocontrol agent WS20 was prepared by homogenizing the fermentation broth ($9.28 \times 10^9$ cfu/mL) of *B. astrophile* ZY1825 with the mixed adjuvants at a volume ratio of 2 : 1. The film-forming time of WS20 was 1.45 min, the coating uniformity was 93.06% and its shelf life was up to 150 days. The stability of heat storage and low temperature followed the national standards of seed treatment suspension agents and microbial formulations. The control effect on cabbage wilt was 64.94% when the cabbage seeds were coated with WS20 at a mass ratio of 1 : 30. The results can provide a reference for the preparation of seed treatment agents and biological control of soil-borne diseases by *Bacillus*.

**内容详见：**

梁玉婷，任兴平，李惠霞，高有军，张海英*，刘永刚*. 生防芽孢杆菌种子处理剂 WS20 的研制及对甘蓝枯萎病的防治效果 [J]. 农药学学报, 2024, 26(3): 482-491.

LIANG Yuting, REN Xingping, LI Huixia, GAO Youjun, ZHANG Haiying*, LIU Yonggang*. Development of biocontrol *Bacillus* seed treatment agent WS20 and control efficacy against cabbage *Fusarium* wilt[J]. Chin J Pestic Sci, 2024, 26(3): 482-491.