◆ 专论：纳米农药青年论坛（特约稿）◆

纳米材料在农药污染治理中的应用研究进展

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摘要：农药作为农业生产中必不可少的生产资料，对农业发展和人类粮食供给做出了巨大贡献，但其使用量的增加导致农药污染问题日益严重。农药污染不仅严重影响农业生产，而且对环境生物和人类健康构成潜在威胁。因此，农药污染治理刻不容缓。纳米材料在农药污染治理中因其高效、可控和环保备受关注。为探讨纳米材料在农药污染治理中的优势与不足，本文综述了纳米材料在农药污染治理中的应用，分析了纳米材料在农药污染治理中的发展现状，以期为今后纳米材料治理农药污染研究提供借鉴。

关键词：纳米材料；农药污染；治理；应用现状

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Research progress on the application of nanomaterials in pesticide pollution control

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Abstract: Pesticides, as indispensable means of production in agricultural production, have made tremendous contributions to agricultural development and human food supply. However, their increased use has led to the increasingly serious pesticide pollution problem. Pesticide pollution not only seriously affects agricultural production, but also poses a potential threat to environmental organisms and human health. Therefore, the control of pesticide pollution is extremely urgent. Nanomaterials have attracted much attention in the control of pesticide pollution due to their high efficiency, controllability, and environmental friendliness. To explore the advantages and disadvantages of nanomaterials in pesticide pollution control, this paper reviewed the application of nanomaterials in pesticide pollution control and analyzed the current development situation of nanomaterials in pesticide pollution control, with the expectation of providing reference for future research on the control of pesticide pollution by nanomaterials.

Key words: nanomaterial; pesticide pollution; control; research progress

农药作为不可或缺的农业生产资料，在提高农作物产量、保障全球粮食安全中发挥着重要作用[1]。据联合国粮农组织FAOSTAT数据库统计，2022年，全球农用农药的使用总量达370万吨（折活性成分），

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比2021年增加4%，比10年前增加13%，是1990年的2倍。然而，农药的大量使用也给水体、土壤以及农产品带来了污染，对环境生物和人类健康构成潜在威胁[2-4]。因此，农药污染治理刻不容缓。

近年来，基于纳米材料的农药污染治理技术因其高效、可控、环保受到广泛关注。纳米材料起源于20世纪70年代，是指三维空间中至少有一维达到纳米尺寸（1～100 nm）或由它们为基本单元组成的材料[5-6]。与传统的治理材料相比，纳米材料具有比表面积大、吸附能力强、反应活性高等优点，因此能够使治理过程更加迅速、有效和精准。本文综述了目前国内外应用于水体、土壤和农产品农药污染治理中的纳米材料（图1），探讨了纳米材料在农药污染治理中的优势与不足，并对未来发展方向进行展望，以期为今后纳米材料治理农药污染研究提供借鉴。

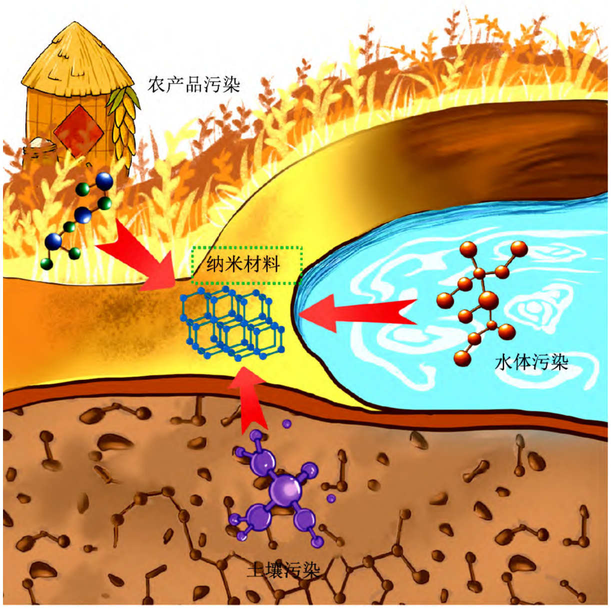

图 1　纳米材料用于治理土壤、水体和农产品农药污染

1　纳米材料在水体农药污染治理中的应用

农药施用后可通过农业排水、雨水冲刷等多种途径进入水体，污染水资源[7]。被农药污染的水体不仅对水生生态系统造成破坏，而且对农业生产、人体健康构成巨大威胁[8]。对于水生生态系统，农药残留可直接毒害鱼类、两栖类及浮游生物，进而破坏食物链，引发生态系统失衡；对于农业生产，灌溉水源受到污染，易对作物造成药害，降低产量；对于人体，长期接触被农药污染的水可诱发癌症、内分泌失调及发育障碍，据FAO统计，全球每年约200万人因农药暴露而患病，其中30%与水体农药污染相关。因此，水体农药污染治理意义重大。

1.1　金属氧化物纳米材料

金属氧化物纳米材料因具有表面活性位点丰富、多孔结构发达、制备方法多样、可修饰性强等优势，在水体农药污染治理领域应用广泛[9-10]。目前，常用于水体农药污染治理的金属氧化物纳米材料主要包括纳米二氧化钛（TiO_2）、纳米四氧化三铁（Fe_3O_4）、纳米氧化锌（ZnO）、纳米氧化铜（CuO）[11]。

纳米TiO_2具有光催化活性高、化学稳定性强、无毒害、制取方法简便、成本低等优点，在金属氧化物纳米材料治理水体农药污染中最具潜力。纳米TiO_2作为光催化剂降解农药的机理是其在光照射下产生电子-空穴对，进而生成强氧化性的羟基自由基（·OH）和超氧自由基（$·O_2^-$），将农药中的化学键破坏，最终实现农药降解。其过程如图2所示[12-14]。Affam等[13]以紫外灯（365 nm）为光源，纳米TiO_2（1.5 g/L）为光催化剂降解水中毒死蜱、氯氰菊酯和百菌清，照射5 h后化学需氧量（COD）去除率达到25.95%，总有机碳（TOC）去除率达到8.45%。然而，在实际应用中纳米TiO_2面临很多问题，主要包括：⑴ 禁带宽度大，可见光响应差；⑵ 光生电子-空穴对复合率高；⑶ 表面反应活性位点不足；⑷ 在反应体系中的分离回收困难。通常情况下，对纳米TiO_2进行形貌调控、掺杂、与其他材料复合等手段可以克服以上部分问题，从而提高纳米TiO_2的光催化效率。例如，Cui等[15]利用*D*-半胱氨酸和金纳米颗粒修饰纳米TiO_2，在最佳条件下对4种有机磷农药（毒死蜱、甲基毒死蜱、马拉硫磷、对硫磷）的降解率均达96.7%。Huong等[14]选择银作为掺杂剂，在太阳光照射下，银掺杂纳米二氧化钛（Ag-TiO_2）能有效分解92.8%的克百威，这一数值显著高于纳米TiO_2（21.3%），且Ag-TiO_2展现出良好的可重复使用性，3次循环后降解效率仍保持在88%以上。

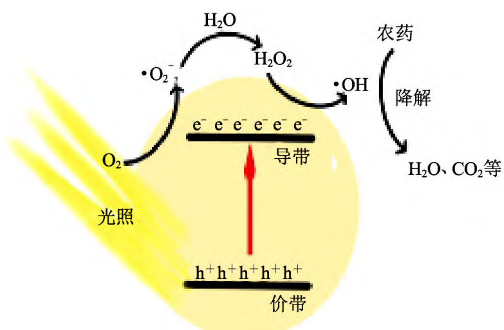

图 2　纳米 TiO_2 光催化降解农药机制[12-14]

纳米Fe_3O_4在水体农药污染治理中兼具吸附和

催化功能。在物理吸附方面，Boruah等[16]构建了Fe_3O_4/还原型氧化石墨烯（rGO）复合材料，可高效吸附去除水中的三嗪类农药。当溶液pH为5时，Fe_3O_4/rGO对莠灭净、扑草净、西玛津、莠去津的吸附率分别为93.61%、91.34%、88.55%、75.24%。在化学催化方面，纳米Fe_3O_4表面Fe^{2+}可通过芬顿反应（$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+ \cdot OH+OH$）产生活性自由基来降解农药污染物，机制如图3所示[17-18]。Shoiful等[19]将纳米Fe_3O_4应用于水中有机氯农药的治理，反应12 h后，林丹、滴滴涕和艾氏剂的降解率分别达到100%、81%、79%。此外，纳米Fe_3O_4具有磁性，吸附剂能够快速简单地从溶液中分离回收，有效避免了二次污染[20]。

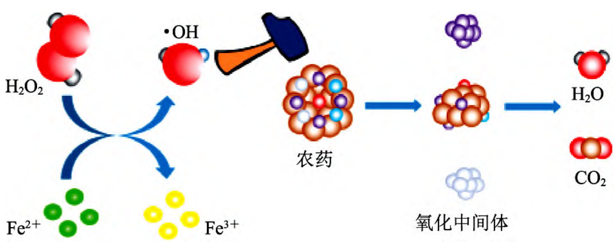

图 3　纳米 Fe_3O_4 催化降解水体农药[17-18]

纳米ZnO在紫外光照射下具有优异的光催化性能，其带隙较宽（3.37 eV），可生成强氧化性自由基，高效降解水体中的农药残留[21]。纳米ZnO作为光催化剂，在紫外光下有机磷农药的降解效率在80%～99.9%[22]。然而，纳米ZnO的应用存在以下问题：(1) 较宽的禁带宽度和高电子空穴对结合能，只能被紫外光激发，导致其只能在紫外光照下发挥高效降解性能；(2) 容易团簇，降低了其催化降解活性。因此，在应用中纳米ZnO需配合其他材料或改变形态，以增强可见光吸收并防止纳米颗粒聚团。Serrano-Lazaro等[23]通过喷雾热解法制备了具有纳米花形态的ZnO薄膜，薄膜中存在的大量天然缺陷增强了可见光吸收，在模拟太阳光照射下，ZnO纳米花可产生大量·OH自由基进而高效降解双硫磷，使其降解半衰期从8.5 h缩短至1.2 h（效率提升7倍）。Hanh等[24]通过引入Cu掺杂，创造了可将电子从价带激发到导带的中间带，从而缩小了ZnO带隙宽度，增强了ZnO光吸收，提高了ZnO光催化活性。即使在可见光照射下，Cu掺杂纳米ZnO也可将久效磷完全降解为CO_2、H_2O和无害的无机离子。

纳米CuO同样可以通过光催化反应降解水体中的农药残留。与块状CuO相比，纳米CuO具有更小的粒径、更大的比表面积；而且，由于其表面存在少量缺陷，这些缺陷可成为活性较高的活性位点。因此，纳米CuO拥有更高的催化活性。研究发现，纳米CuO在碱性条件下（pH=9）对吡虫啉的降解率高达99%[25]。此外，CuO是一种窄带隙的p型半导体，可使宽带隙氧化物的光捕获量增加、电子转移加快，进而增强宽带隙氧化物的光催化降解性能。Basaleh等[26]采用溶胶-凝胶法制备了不同CuO含量的可回收纳米材料CuO-YVO_4（钒酸钇），CuO的加入显著增强了YVO_4光催化活性。当CuO的质量分数为15%时，可完全降解水体中的莠去津。

1.2　碳基纳米材料

碳基纳米材料不仅能够通过孔填充、氢键作用、π-π相互作用等机制吸附去除水体中的农药污染物，还可通过光催化或化学催化实现农药的降解[27-29]。常用于水体农药污染治理的碳基纳米材料包括石墨烯、碳纳米管、碳量子点。其特性如表1所示[30-32]。

表 1　水体农药污染常用碳基纳米材料及其特性

材料类型	代表材料	特性与优势
石墨烯	氧化石墨烯（GO）、还原型氧化石墨烯（rGO）	单层二维结构、丰富的含氧官能团、高机械强度，可通过π-π作用吸附农药
碳纳米管	单壁/多壁碳纳米管（SWCNT/MWCNT）	高比表面积、中空管状结构、优异的电子传导性，可通过表面修饰增强选择性，具有强吸附作用
碳量子点	氮掺杂碳量子点（N-CQDs）	荧光特性、高光催化活性、低毒性，适用于光催化降解与污染物检测

石墨烯及其衍生物（GO、rGO）具有独特的结构特性和优异的物理化学性质，可高效吸附水体中的农药[33]。Maliyekkal等[34]研究发现，rGO对水中毒死蜱、硫丹和马拉硫磷的吸附量分别高达1 200、800、1 100 mg/g 。此外，GO、rGO可通过金属掺杂大幅增强其对农药污染的治理效率。Koushik等[35]将银（Ag）掺入到rGO中，显著增强了rGO去除硫丹、毒死蜱的效率，去除机制可归因于Ag纳米颗粒对目标污染物进行脱卤，然后通过石墨烯表面π-π相互作用吸附其降解的化合物，机制如图4所示。

碳纳米管（CNTs）根据结构可分为单壁碳纳米管（SWCNTs）和多壁碳纳米管（MWCNTs），其中SWCNTs的直径通常为1～2 nm，而MWCNTs的直径则分布在5～50 nm[36-38]。研究表明，SWCNTs对有机

农药具有显著的吸附能力。De Martino等[31]研究发现，SWCNTs对2甲4氯（MCPA）的吸附量可达25.7 mg/g。此外，CNTs可与金属氧化物配合，构建纳米复合材料，进一步提升吸附性能。Lung等[36]将MnO_2、Fe_3O_4纳米颗粒与SWCNTs复合，对敌草胺和三唑酮具有良好的吸附效果，最高吸附量分别达到20.492、14.706 mg/g。值得注意的是，表面改性也会提高CNTs的吸附性能。Deng等[39]将SWCNTs表面进行硝酸酸化处理，引入了羧基基团，进而增加了SWCNTs的表面积和孔隙体积，增强了对敌草隆的吸附能力。

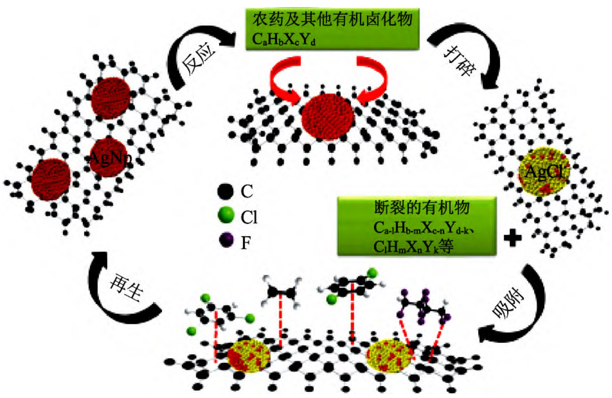

图4 rGO@Ag治理农药污染机制图[35]

碳量子点（CQDs）因其独特的荧光特性和光催化活性，在农药检测与污染治理中展现出广阔的应用前景。一方面，其荧光响应可用于实时监测农药浓度变化；另一方面，在光照条件下能高效催化降解农药。近年来，碳量子点的表面功能化改性研究取得了重要突破。通过精心调控其表面结构（如缺陷位点钝化修饰和特异性功能基团引入），可显著增强其光催化活性。Targhan等[40]开发的巯基功能化碳量子点（CQD-SH）在水环境中对吡虫啉展现出卓越的光催化降解性能，在可见光照射条件下仅需90 min即可实现90.13%的高效降解。这项研究为设计高效水处理光催化剂提供了新的思路。此外，构建CQDs基纳米复合材料是另一种有效策略，如采用水热法合成的$Al_2(SO_4)_3$/CQDs（5% CQDs、95% $Al_2(SO_4)_3$）复合物（2～10 nm），在可见光照射60 min后对氟虫腈的降解率达84%[41]。然而，相比于光催化降解，CQDs因高灵敏度、优良的可调荧光特性，在农药残留检测领域的研究更为广泛，具有更大的发展潜力。

1.3 金属纳米材料

金属纳米材料[纳米零价铁（nZVI）、纳米零价铜（nCu）等]因其优异的催化性能在环境污染治理领域备受关注。这类材料具有以下突出特性：(1) 强还原性使其可有效降解氧化态污染物；(2) 纳米级粒径赋予材料更大的比表面积和丰富的活性位点；(3) 金属-污染物界面的高效电子转移能力显著提升催化效率。这些特性使得金属纳米材料在难降解污染物特别是农药污染物的治理中展现出显著优势[42]。

nZVI是指粒径在1～100 nm的零价铁颗粒[43]。近10年，nZVI因其比表面积大、还原性强等优势已在农药污染治理领域中发挥了重要作用[44]。Bezbaruah等[45]利用nZVI治理水体中的甲草胺，发现甲草胺在72 h内降解率达92%。nZVI还是一种良好的铁基类Fenton催化剂，可通过类Fenton反应降解农药[46]。Sun等[17]发现，nZVI/H_2O_2体系可降解马拉硫磷，其降解率1.5 h内高达98%。在同样条件下，nZVI/H_2O_2体系也可快速降解茚虫威，在15 min内实现了96.5%的降解[47]。而单独使用nZVI，极易导致颗粒的团聚与氧化，导致nZVI失活。因此，在应用中nZVI负载于载体材料（如硅藻土、蒙脱石等），以提升其稳定性与实用性[45]。Ding等[48]将nZVI负载到蒙脱石上，有效抑制了nZVI颗粒的团聚与氧化，在温度为35℃、pH为3的最佳条件下，对水体中噻虫嗪的去除效率高达94.29%。Khodabakhshi等[49]分别使用浮石-纳米零价铁（P-nZVI）、硅藻土-纳米零价铁（D-nZVI）复合材料去除水溶液中百草枯，在最佳条件（pH 3.74）下，P-nZVI和D-nZVI对百草枯的去除效率分别为85.28%、92.76%。

nCu因其高还原电势和催化活性，在有机磷农药降解中表现突出。Saleem等[50]研究发现，nCu可将甲基对硫磷水解为对硝基苯酚，降解率在4 h内可达85%。此外，nCu还可与光催化材料（如TiO_2）复合，通过抑制光生载流子复合、拓宽光响应范围，从而增强光催化降解性能。nCu/TiO_2复合材料在可见光下对毒死蜱的降解效率较单一材料提高40%[29]。与nZVI相比，nCu应用到水体农药污染治理领域的实例较少，原因可能是nCu的负载难度高，应用不当容易造成水体重金属污染。

1.4 金属有机框架材料(MOFs)

MOFs是由无机金属中心（金属离子或金属簇）与有机配体通过自组装形成的一类具有网络结构的晶态多孔材料[51-53]。该类材料具有比传统多孔材料更大的比表面积、更高的孔隙率，同时由于有机成分的存在又使其兼具可设计性、可剪裁性、孔道尺寸可调节性、孔道表面易功能化等特点，在水体

农药污染治理领域取得众多研究成果。但是，因为金属中心与配体分子之间的配位键不稳定，许多MOFs在水环境中容易发生水解，导致骨架崩塌[54-55]。为了提高MOFs的稳定性，通常从改变金属团簇、修饰有机配体、引入稳定模块等3个方向入手。

高价金属离子（如Zr^{4+}、Fe^{3+}、La^{3+}）优先与O供体（硬碱）配位，形成的MOFs具有更好的稳定性[56]。Alkhatib等[57]设计了一种镧系金属有机框架（La-MOFs），可在水溶液中稳定存在并高效吸附溴氰菊酯，在pH为4时，吸附率高达95.8%。根据HSAB原理，稳定的MOFs还可以由软二价金属离子（如Zn^{2+}、Cu^{2+}、Ni^{2+}、Mn^{2+}、Ag^{+}）和软偶氮配体（如咪唑酸盐、吡唑酸盐、三唑酸盐、四唑酸盐）组装而成。Yang等[58]发表了关于ZIF（沸石咪唑酯骨架结构材料）的论文，报道了ZIF结构的8种拓扑结构。其中，ZIF-8显示出较强的热稳定性和化学稳定性。研究表明，ZIF-8可稳定治理水体中的有机磷类农药、苯基吡唑类农药、酰胺类农药等[59-63]。相较于单一金属MOFs，多金属MOFs更强的稳定性赋予其更高的治理效率。原因主要有：⑴ 形成了更强的配位键；⑵ 增强了金属团簇的惰性；⑶ 提高了表面疏水性[58, 64]。Yang等[65]2023年报道，双金属有机框架MOF-808（Zr/Ce）具有有机磷水解酶活性，对水中丙溴磷的降解率达到了95%。

修饰MOFs有机配体，主要通过引入疏水基团，以降低MOFs对水的亲和力，保护弱配位键免受水分子的攻击，以增强MOFs在水中的稳定性和污染治理效率[54, 66]。Chen等[67]发现，基于Cu^{2+}的金属有机框架（CP-MOF）缺乏稳定性，但通过引入羧酸盐配体制备的CP-MOF，具有高配位连接（8位）、丰富的疏水基团（6个甲基）和稳定的集合性状（四面体架构），即使在水中放置10 d仍保持结构完整性，并且对酰胺类农药、有机磷类农药具有高吸附能力。

引入稳定模块，使用聚合物或纳米颗粒形成保护层来提高MOFs的稳定性[68-69]。Wan等[70]构建了一种Fe_3O_4@ZIF-8@polymer的材料，功能聚合物涂层的添加大大提高了ZIF-8的水体稳定性。试验表明，Fe_3O_4@ZIF-8@polymer对9种有机磷农药具有优异的吸附能力，最高吸附率达到94.3%。

1.5　纳米酶

纳米酶是一类具有酶催化活性的功能纳米材料，集纳米材料特征和酶活性于一体。相较于生物酶，纳米酶克服了生物酶的固有缺点，制备成本低，活性可调控，稳定性好，在水体农药污染治理方面具有巨大应用价值[71-72]。大多数纳米酶通过结构设计可精确模拟过氧化物酶（POD）、氧化酶（OXD）、过氧化氢酶（CAT）和超氧化物歧化酶（SOD）等氧化还原酶的活性，其中一小部分具有与水解酶或其他酶相似的催化能力[73-74]。

Yang等[75]构建了一种具自调节pH和自供应H的纳米酶（CP@CA），即柠檬酸修饰纳米CuO_2，合成路径如图5所示。CP@CA可高效降解水体中7种磺酰脲类除草剂，其中对烟嘧磺隆的降解效果极佳，56 min内降解率高达97.58%。Chen等[76]用Fe纳米颗粒掺杂富N多孔碳，构建出一种具有氧化酶催化活性的纳米酶，能够高效催化以分子氧为电子受体的氧化反应，可治理水中有机磷类农药，其中对毒死蜱的治理效率最高，达到91.4%。

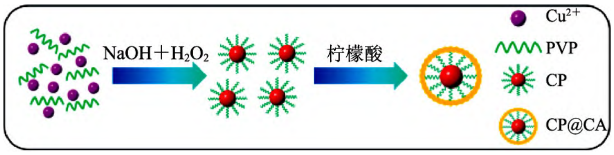

图 5　CP@CA 纳米酶合成路径图

2　纳米材料在土壤农药污染治理中的应用

土壤是农药在环境中的“贮藏库”与“集散地”，超过80%的农药施用后最终进入土壤[77-78]。农药在土壤中容易发生化学反应，影响土壤中的微生物群体、植物根系和土壤结构，导致土壤质量下降。首先，农药进入土壤后很快与土壤中的微生物、有机质等反应，导致微生物数量减少，生态平衡受到破坏，使土壤肥力减弱，植物生长受到限制。其次，农药在土壤中的残留时间较长，有些农药的残留期甚至可达数年之久，这种现象导致土壤中的有机质水平下降，土壤质量降低，最终导致生态环境受到破坏。与水体农药污染相比，土壤农药污染环境特性（隐蔽分布、持久残留特性和生物累积效应）复杂，治理难度更大[79-81]。

2.1　金属氧化物纳米材料

纳米TiO_2和纳米ZnO作为光催化剂，已被证明可加速土壤中农药的光降解。El-Saeid等[82]模拟了莠去津、毒死蜱、乐果、七氯和灭多威在真实土壤系统中的光降解。试验显示，在纳米TiO_2、纳米ZnO存在下，降解速率均提高60%以上。不可避免的是，在土壤环境中，光催化剂依赖紫外线的问题被放大。解决该问题，可从以下方面入手：⑴ 通过配合其他材料拓宽其光响应范围，如氮元素掺杂改性的TiO_2（N-TiO_2）可显著提升莠去津的降解效率，较未改性

TiO_2提高了40%以上[83-84]；(2) 将光催化剂固定在土壤表面，如利用N-TiO_2与g-C_3N_4（类石墨相氮化碳）复合材料（N-TiO_2/g-C_3N_4）对聚乳酸地膜（PLA-MF）进行改性，将该地膜覆盖于地表后，可通过光催化作用降解土壤中的多菌灵（CBD），降解率达60%[85-86]；(3) 配合农药降解菌株增强降解效率，如纳米TiO_2与土壤菌株CDS-8结合后形成的复合体系可高效降解土壤中的百菌清，静态条件下百菌清的降解率为94.94%，人工翻耕处理后降解率进一步提升至97.55%[87]。然而，纳米金属氧化物易与土壤中有机物相互作用，对土壤生物（如蚯蚓）产生一定的影响[88]。为解决该问题，Daqa等[89]利用沉淀工艺构建了壳聚糖包覆的纳米ZnO（chitosan-ZnO），壳聚糖涂层的存在，有效阻止了纳米ZnO与土壤有机物相互作用，并且chitosan-ZnO可高效降解噻呋酰胺和苯醚甲环唑，两者在沙壤土中72 h降解率分别高达92.0%和93.1%。

Fe_3O_4纳米颗粒作为一种多功能纳米材料，在土壤农药污染治理中展现出独特的综合优势：(1) 改善光催化剂的结构和光催化活性。Xu等[90]采用溶液-凝胶法制备了Fe_3O_4/SiO_2/TiO_2光催化剂，该材料以纳米Fe_3O_4为胶体核心，表现出优异的光催化性能，可高效降解土壤中的草甘膦，2 h内降解率高达89%。(2) 具有超顺磁性以便于回收。Kalantar等[91]通过溶剂-凝胶法合成了ZnO/Fe_3O_4纳米颗粒并用于土壤中二嗪磷催化降解，其降解率高达99.3%，并且ZnO/Fe_3O_4纳米颗粒具有超顺磁性和矫顽力场，便于该材料的回收。(3) 与土壤微生物相互作用，激活土壤微生物降解农药的潜力。Fang等[92]发现纳米Fe_3O_4可结合土壤原生微生物降解土壤中2,4-滴，纳米Fe_3O_4的存在，显著提高了土壤微生物降解2,4-滴的效率。(4) 丰富的Fe^{2+}/Fe^{3+}氧化还原对，促进了土壤农药氧化还原降解。Bai等[93]构建了农药降解催化剂Fe_3O_4@Fe(0)-漆酶，以2,2'-联氮-双-3-乙基苯并噻唑啉-6-磺酸（ABTS）作为助催化剂，助催化剂的加入加速了Fe_3O_4中Fe^{2+}/Fe^{3+}循环，从而提高了氧化电位，进而使Fe_3O_4@Fe(0)-漆酶加速降解土壤中甲氧滴滴涕，降解率达88%。

2.2　碳基纳米材料

碳基纳米材料（如石墨烯）因其具有大量活性位点，可激活过硫酸盐，产生硫酸根自由基（$SO_4^{\cdot -}$）以治理土壤农药污染。Shu等[94]制备了一种nZVI负载的氮掺杂还原型氧化石墨烯（N-rGO）复合材料（nZVI@N-rGO），并将其用于活化过氧二硫酸盐（PDS）以去除污染土壤中的六六六（HCH），8 h后六六六的去除效率高达95.4%。

然而，土壤系统的复杂性限制了碳基纳米材料的广泛应用。碳基纳米材料不仅会与污染物相互作用，还会与土壤组分相互影响。(1) 碳基纳米材料在土壤颗粒上的固定会限制其表面对农药的吸附性；(2) 土壤组分会与农药竞争碳基纳米材料的吸附位点，进而影响吸附性能；(3) 碳基纳米材料在土壤中的迁移会改变其在土壤中的分布，难以回收。因此，在设计碳基纳米材料时，考虑其与土壤的相互作用至关重要[95]。

2.3　金属纳米材料

nZVI广泛应用于土壤有机氯农药的治理[96-98]。Han等[98]发现，nZVI能大大缩短滴滴涕在土壤中的半衰期，当nZVI添加量为0.5%～2%时，滴滴涕的降解半衰期从58.3 h显著缩短至27.6 h。然而，nZVI在土壤中易氧化或团聚而失活，通过表面包覆（如羧甲基纤维素）或负载于多孔载体（如生物炭），可大大提高nZVI在土壤中的稳定性[43]。Li等[99]制备了一种负载花生壳生物炭的纳米零价铁材料（BC/nZVI），可高效降解土壤中的滴滴涕和林丹，降解率分别达到55.2%和85.4%。

nCu在土壤中可高效降解有机磷农药，使其转化为低毒代谢产物。Chen等[100]构建了一种磷酸三酯酶（PTE）-Cu花状纳米颗粒，其催化降解有机磷农药效率是游离PTE的1.76倍。此外，有研究指出，nCu在土壤中吸附农药的效率与土壤成分密切相关，Tortella等[101]发现，nCu在低有机质土壤中吸附多菌灵与异菌脲的效率远高于在高有机质土壤中。

2.4　金属有机框架材料

MOFs在土壤中表现出优异的吸附性能，可选择性地吸附特定类型的农药污染物[102]。He等[103]构建了一种绿色植物基Bi-Zr双金属MOF SU-101.2，可特异性吸附土壤中三唑酮，吸附机制包括静电相互作用、氢键和π-π相互作用。Almohana等[104]制备了一种金属有机框架/氧化石墨烯（MOF-801/GO）吸附剂，可特异性吸附有机硫农药，其中对福美双的吸附率高达92%。此外，MOFs在土壤中还表现出优异的催化性能[105]。Vigneshwaran等[106]采用溶剂热法构建了TiO_2/壳聚糖/MIL-88复合材料（TCS@MOF），其在30 min内对久效磷的降解率高达98.79%。

然而，MOFs在土壤农药污染治理领域尚未大规模应用，仍存在诸多难点：(1) MOFs坍塌可能释放出Cu^{2+}等重金属离子，影响土壤微生物的活性；

⑵ 非磁性MOFs在土壤中难以分离，传统淋洗回收率仅有20%～40%；⑶ MOFs再生过程需有机溶剂（如甲醇等），可能引发二次污染。因此，未来研究方向主要有以下几方面：⑴ 筛选生物相容性MOFs（如Fe基、Ca基），减少金属毒性风险；⑵ 通过凝胶包裹或黏土负载限制MOFs的迁移，并延长其在复杂环境中的稳定性与长效性；⑶ 构建pH/光双响应MOFs，实现农药靶向吸附与触发式降解；⑷ 利用农业废弃物（如秸秆）提取的有机配体替代传统的石油基配体[107-109]。

3　纳米材料在农产品农药污染治理中的应用

随着农产品（粮食、水果及蔬菜）的规模化种植步伐加快，其对农药的依赖性越来越高。多种类、高剂量的农药被广泛用于缩短生长周期以及防治病虫害，农药残留超标现象在食品检测中时有发生[110]。根据国家市场监督监测数据，2021年食品抽检不合格项目中，农药残留超标占26.38%[111]。农产品中的农药残留直接威胁食品安全与消费者健康。传统方法，如清洗、浸泡和化学脱除，常面临降解效率低、二次污染及营养损失等问题[112]。纳米材料可根据不同情况，针对性地设计优化以实现农产品残留农药的精准去除，同时最大程度保留农产品的品质特性，是未来食品安全保障领域的重要方向。

TiO_2纳米颗粒可用于治理农产品表面农药残留（图6）。Inprasit等[113]发现，TiO_2与聚乙二醇（PEG 6000）结合可高效降解韭菜中的多菌灵，在最优处理条件（TiO_2质量浓度为1.0%～1.5%，PEG 6000添加量为2%）下，可实现90%以上的光催化降解效率。

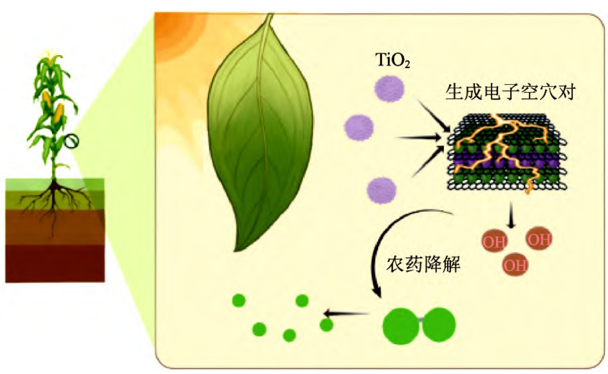

图 6　TiO_2 光催化剂用于降解农产品表面农药残留

磁性Fe_3O_4纳米颗粒可通过负载表面活性剂（如β-环糊精）形成疏水空腔，有效识别并吸附果蔬表面的有机氯农药。结合磁场辅助分离技术，该体系还可实现快速回收。试验表明，Fe_3O_4/β-环糊精清洗剂对菠菜中林丹的去除率较传统洗涤剂提高了40%，且可回收再利用[114-116]。

碳基纳米材料凭借其无毒、易分离等优势，可吸附去除农产品表面残留农药[115-116]。例如，Markus等[117]成功开发了一种基于磁铁矿-孢粉素/氧化石墨烯的新型磁性吸附剂（Fe_3O_4-SP/GO），可用于吸附蔬菜（青椒、黄瓜等）表面残留的乐果、稻丰散和磷胺。

纳米材料在农产品农药残留治理领域的研究仍处在起步阶段。在未来的研究中，需建立严格的纳米材料迁移与回收标准，确保处理后产品无纳米颗粒残留风险；结合物联网技术开发智能清洗设备，实现农药残留实时监测与纳米材料剂量精准调控。

4　结论与展望

纳米材料因其独特的物理化学性质（如高比表面积、优异的催化活性及可控的表面功能化特性），在农药污染治理领域展现出广阔的应用前景。通过吸附、光催化、还原降解等机制，纳米材料在水体、土壤及农产品农药污染治理中取得显著进展，成为传统治理技术的重要补充与革新方向。

然而，纳米材料的实际应用仍面临多重挑战。首先，在复杂环境介质（如高有机质土壤、异质水体）中，纳米颗粒易团聚或失活，活性受pH、光照等条件制约。其次，部分纳米材料成本较高，规模化制备与精准投放技术尚未成熟，且可能引发生态风险（如金属离子溶出、生物累积）。最后，农药降解中间产物的毒性评估及纳米材料在食物链中的迁移规律研究仍不充分，制约了其安全应用。这些问题的解决需要多学科交叉研究与系统性风险评估。

未来研究应侧重以下方向：⑴ 开发环境响应型智能纳米材料，如光/酶双驱动纳米催化剂，提升复杂场景适应性；⑵ 优化绿色合成工艺，利用农业废弃物开发生物质基纳米材料以降低成本；⑶ 加强复合纳米材料的界面工程设计与稳定性调控，降低二次污染风险；⑷ 构建“纳米材料-微生物-植物”协同修复体系，实现污染物定向转化与生态功能恢复；⑸ 完善纳米材料全生命周期评估体系，建立国际标准化的安全性数据库。随着材料科学与环境工程的深度融合，纳米技术有望推动农药污染治理向高效化、精准化与可持续化方向发展，为全球农业生态安全提供技术支撑。

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