Notice

DESCRIPTION CN117623388A

A method for pesticide residue degradation based on 3D molybdenum disulfide nanoflower materials

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一种基于3D二硫化钼纳米花材料的农残降解方法

[0001]

Technical Field

技术领域

[n0001]

This invention belongs to the field of pesticide residue degradation, specifically relating to a method for pesticide residue degradation based on 3D molybdenum disulfide nanoflower materials.

本发明属于农残降解领域，具体涉及一种基于3D二硫化钼纳米花材料的农残降解方法。

[0003]

Background Technology

背景技术

[n0002]

The information disclosed in this background section is intended only to enhance understanding of the overall background of the invention and is not necessarily to be construed as an admission or in any way implying that such information constitutes prior art known to those skilled in the art.

公开该背景技术部分的信息仅仅旨在增加对本发明的总体背景的理解，而不必然被视为承认或以任何形式暗示该信息构成已经成为本领域一般技术人员所公知的现有技术。

[n0003]

The safety of fruits, vegetables, and agricultural products is of paramount importance in my country's food safety system.

果蔬农产品的食用安全，在我国食品安全中占有极其重要的地位。

The use of pesticides has become the main means of ensuring and stabilizing the production of fruits and vegetables, but the problem of excessive pesticide residues caused by unscientific use of pesticides is prominent.

农药的使用已成为果蔬保产稳产的主要手段，但不科学用药等造成的农残超标问题突出。

The high detection rate of neonicotinoid insecticides in fruits and vegetables seriously affects human health and import/export trade.

新烟碱类杀虫剂在果蔬中检出率高，严重影响了人体健康和进出口贸易。

Pesticide residues on the surface of fruits and vegetables are the main reason for their excessive pesticide residues. Due to the differences in the physicochemical properties of pesticides, the edible parts of fruits and vegetables, and the surface structure characteristics, existing methods are difficult to meet the needs of pesticide residue removal in multiple scenarios.

果蔬表面农药残留是造成其农残超标的主要原因，由于农药物理化学性质、果蔬食用部位及表面结构特性等的差异，现有方法难以满足多场景下的农残去除需求。

[n0004]

Tomato (Solanum lycopersicum L.)

番茄(Solanum lycopersicum L.)

It is a dual-purpose crop, used as both a vegetable and a fruit, rich in vitamin C, lycopene, carotenoids, and flavonoids, and is widely cultivated and consumed.

是一种富含维生素C、番茄红素、类胡萝卜素和类黄酮的蔬菜水果两用作物，被广泛种植和食用。

Because tomatoes are highly susceptible to pests and diseases during growth and storage, pesticides are used extensively. Tomatoes are one of the three vegetables with the highest pesticide detection rates. Tomatoes have a distinctive aroma and are a ready-to-eat vegetable. About one-third of tomatoes are eaten fresh, which greatly increases the potential risk of exposure through dietary intake. In addition, the application of pesticides has been shown to affect the aroma and quality of tomato fruits. Therefore, researching new, efficient, safe, and widely applicable methods for degrading pesticide residues in fruits and vegetables is of great significance for ensuring the safety of fruits and vegetables.

由于番茄在生长和储存过程中极易受到病虫害侵染，因此农药被大量使用。 番茄是农药检出率最高的三大蔬菜之一。 番茄具有独特的香气，是一种即食蔬菜，约有三分之一的番茄是新鲜食用的，这大大增加了通过饮食摄入暴露的潜在风险。 此外，农药的施用已被证明对番茄果实的香气品质有影响。 因此，研究高效、安全、适用性强的果蔬农药残留降解新方法，对保障果蔬食品安全具有重要意义。

[n0005]

In recent years, methods including washing, peeling, and blanching have been used to remove pesticide residues from fruits and vegetables.

近年来，包括洗涤、去皮、焯水等在内的方法被用于果蔬中农药残留的去除。

Washing is the simplest and most economical method, suitable for both home and industrial-scale food processing. Washing can also effectively prevent the waste of nutrients during fruit peel processing. In addition, washing techniques including ozone, ultrasound, water electrolysis, or chemical solutions (such as HO and chlorine compounds) have also been reported as effective methods for removing pesticide residues from food. The technology of catalyst-activated persulfate degradation of pollutants has recently been applied to the removal of pesticides in water. For example, patent CN113716671A discloses a method for treating wastewater based on 1T phase nano molybdenum disulfide and the preparation method of the 1T phase nano molybdenum disulfide. It utilizes 1T phase nano molybdenum disulfide and persulfate to degrade neonicotinoid pesticides under low pH conditions. Because of its demanding degradation conditions, it requires low pH (pH=1-3) to achieve a high degradation effect on neonicotinoid pesticides, and the degradation rate can only reach 70% after 180 minutes. Therefore, it cannot be applied to the degradation of pesticide residues in fruits and vegetables, and the effect of this treatment on the aroma and quality of fruits and vegetables has not yet been studied.

其中，洗涤是最简单和经济的方法，适用于家庭和工业规模的食品加工过程。 清洗还能有效避免果皮加工过程中营养物质的浪费。 此外，包括臭氧、超声波、电解水或化学溶液(如H₂O₂和氯化合物)在内的洗涤技术也被报道为去除食品中农药残留的有效方法。 催化剂活化过硫酸盐降解污染物的技术近来被应用于水中农药的去除，如专利CN113716671A公开了一种基于1T相纳米二硫化钼处理废水的方法及该1T相纳米二硫化钼的制备方法，其利用1T相纳米二硫化钼和过硫酸盐在低pH条件下降解新烟碱类农药。 因其降解条件苛刻，需要在低pH(pH＝1～3)下才能对新烟碱类农药有较高的降解效果，180min降解率才能达到70%，无法应用到果蔬农药残留降解中，且该处理对果蔬香气品质的影响也尚未研究。

[0008]

Summary of the Invention

发明内容

[n0006]

To address the shortcomings of existing technologies, the purpose of this invention is to provide a method for pesticide residue degradation based on 3D molybdenum disulfide nanoflower materials. The 3D molybdenum disulfide nanoflower materials provided by this invention can effectively activate persulfate, rapidly degrade pesticide residues on fruits and vegetables in a short time without damaging the aroma and quality of the fruits and vegetables.

为了解决现有技术的不足，本发明的目的是提供一种基于3D二硫化钼纳米花材料的农残降解方法，本发明提供的3D二硫化钼纳米花材料可有效活化过一硫酸盐，短时间内快速降解果蔬上的农残且不破坏果蔬的香气品质。

[n0007]

To achieve the above objectives, the technical solution of the present invention is as follows:

为了实现上述目的，本发明的技术方案为：

[n0008]

In a first aspect, the present invention provides a method for preparing 3D molybdenum disulfide nanoflower materials, comprising the following steps:

本发明的第一个方面，提供一种3D二硫化钼纳米花材料的制备方法，包括如下步骤：

[n0009]

(1) The molybdenum source and the sulfur source are mixed and dissolved in water to obtain a mixed solution;

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(1)将钼源和硫源混合后溶解在水中，得到混合溶液；

[n0010]

(2) The mixed solution was subjected to a hydrothermal reaction. After the hydrothermal reaction was completed, the product was collected, washed and dried to obtain 3D molybdenum disulfide nanoflower material.

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(2)将混合溶液进行水热反应，水热反应结束后收集产物，洗涤并干燥，得到3D二硫化钼纳米花材料。

[n0011]

In some embodiments of the present invention, the molybdenum source is a molybdate, including but not limited to sodium molybdate and ammonium molybdate.

在本发明的一些实施例中，所述钼源为钼酸盐，包括但不限于钼酸钠和钼酸铵。

[n0012]

In some embodiments of the present invention, the sulfur source is a sulfur-containing compound, including thiourea and thioacetamide.

在本发明的一些实施例中，所述硫源为含硫化合物，包括硫脲和硫代乙酰胺。

[n0013]

In some embodiments of the present invention, the molybdenum source is ammonium heptamolybdate tetrahydrate, and the sulfur source is thiourea; the mass ratio of ammonium heptamolybdate tetrahydrate to thiourea is 1-1.5:2-2.5, g:g.

在本发明的一些实施例中，所述钼源为四水合七钼酸铵，所述硫源为硫脲；四水合七钼酸铵与硫脲的质量比为1～1.5：2～2.5，g：g。

[n0014]

Preferably, the mass ratio of ammonium heptamolybdate tetrahydrate to thiourea is 1.24:2.28 (g:g).

优选的，四水合七钼酸铵与硫脲的质量比为1.24：2.28，g：g。

[n0015]

In some embodiments of the present invention, a molybdenum source and a sulfur source are mixed and dissolved in water, and then stirred to obtain a mixed solution.

在本发明的一些实施例中，将钼源和硫源混合后溶解在水中，搅拌得到混合溶液。

The mixed solution is transferred to a hydrothermal reactor for hydrothermal reaction.

将混合溶液转移至水热釜中，进行水热反应。

To avoid damage to the hydrothermal reactor from high temperatures, a hydrothermal reactor with a polyphenol liner can be used.

为了避免高温度破坏水热釜，可采用聚苯酚内衬的水热釜。

[n0016]

In some embodiments of the present invention, the hydrothermal reaction is carried out at 190–210°C for 10–14 h.

在本发明的一些实施例中，所述水热反应的反应条件为190～210°C下反应10～14h。

[n0017]

In some embodiments of the present invention, after the hydrothermal reaction is completed, the product can be collected by centrifugation.

在本发明的一些实施例中，水热反应结束后，可采用离心的方式收集产物。

The collected product can be washed several times with deionized water and ethanol, and then dried.

对于收集得到的产物，可采用去离子水和乙醇清洗数次，并进行干燥。

[n0018]

The present invention does not limit the drying method of the target product, as long as it can achieve thorough drying.

本发明对目标产物的干燥方式并不进行限定，能够实现彻底干燥即可。

For example, vacuum drying can be used, drying overnight at 60°C.

比如，可采用真空干燥的方式，在60°C条件下烘干过夜。

[n0019]

In a second aspect, the present invention provides a 3D molybdenum disulfide nanoflower material, which is prepared by the above-described preparation method;

本发明的第二个方面，提供一种3D二硫化钼纳米花材料，采用上述的制备方法制得；

[n0020]

The 3D molybdenum disulfide nanoflower material contains a 2H phase and a 1T phase.

所述3D二硫化钼纳米花材料中存在2H相和1T相。

[n0021]

The 3D molybdenum disulfide nanoflower material provided by this invention has a unique flower-like structure and exhibits a unique cornflower-like morphology. The unique flower-like structure is beneficial for the exposure of active sites and improves mass transfer efficiency.

本发明提供的3D二硫化钼纳米花材料具有独特的花状结构，呈现出独特的矢车菊花朵状形貌，独特的花状结构有利于活性位点的暴露并提高传质效率。

Meanwhile, the 3D molybdenum disulfide nanoflower material provided by this invention undergoes a transformation from the 2H phase to the 1T phase.

同时，本发明提供的3D二硫化钼纳米花材料发生了由2H相向1T相的转变。

[n0022]

A third aspect of the present invention provides an application of the above-mentioned 3D molybdenum disulfide nanoflower material in conjunction with persulfate in the degradation of pesticide residues.

本发明的第三个方面，提供一种上述的3D二硫化钼纳米花材料协同过一硫酸盐在降解农残中的应用。

[n0023]

In some embodiments of the present invention, the application is to degrade pesticide residues on fruits and vegetables.

在本发明的一些实施例中，所述应用为降解果蔬上的农残。

[n0024]

Preferably, the fruits and vegetables include, but are not limited to, tomatoes.

优选的，所述果蔬包括但不限于番茄。

[n0025]

In some embodiments of the present invention, the application involves adding the above-mentioned 3D molybdenum disulfide nanoflower material and persulfate to water containing fruits and vegetables.

在本发明的一些实施例中，所述应用为将上述的3D二硫化钼纳米花材料和过一硫酸盐加入含有果蔬的水中。

[n0026]

In some embodiments of the present invention, the pesticide residue is a neonicotinoid pesticide, including but not limited to acetamiprid, imidacloprid, and thiamethoxam.

在本发明的一些实施例中，所述农残为新烟碱类农药，包括但不限于啶虫脒、吡虫啉和噻虫嗪。

[n0027]

A fourth aspect of the present invention provides a method for pesticide residue degradation based on 3D molybdenum disulfide nanoflower materials, comprising the following steps:

本发明的第四个方面，提供一种基于3D二硫化钼纳米花材料的农残降解方法，包括如下步骤：

[n0028]

The above-mentioned 3D molybdenum disulfide nanoflower material was mixed with persulfate and added to water containing fruits and vegetables.

将上述的3D二硫化钼纳米花材料和过一硫酸盐混合，加入含有果蔬的水中。

[n0029]

The pesticide residue degradation method provided by this invention is simple and convenient to operate, and the pesticide residue degradation effect is very good.

本发明提供的农残降解方法操作简单，方便，且农残降解效果非常好。

Specifically, the method of the present invention can achieve rapid degradation of pesticide residues using a small amount of 3D molybdenum disulfide nanoflower material and persulfate. Within 15 minutes, the degradation rates of acetamiprid, imidacloprid and thiamethoxam can reach 97.1%, 95.3% and 100%, respectively.

具体的，本发明的方法可以在使用少量3D二硫化钼纳米花材料和过一硫酸盐的情况下实现农残的快速降解，15分钟内，啶虫脒、吡虫啉和噻虫嗪的降解率可达97.1%、95.3%和100%。

[n0030]

In some embodiments of the present invention, the concentration of 3D molybdenum disulfide nanoflower material in the water containing fruits and vegetables is 0.02-0.04 g/L, and the concentration of persulfate is 0.7-0.9 mM.

在本发明的一些实施例中，所述含有果蔬的水中，3D二硫化钼纳米花材料的浓度为0.02～0.04g/L，过一硫酸盐的浓度为0.7～0.9mM。

[n0031]

In some embodiments of the present invention, the pesticide residue is a neonicotinoid pesticide, including acetamiprid, imidacloprid, and thiamethoxam.

在本发明的一些实施例中，所述农残为新烟碱类农药，包括啶虫脒、吡虫啉和噻虫嗪。

[n0032]

The beneficial effects of this invention are as follows:

本发明的有益效果为：

[n0033]

This invention prepares 3D molybdenum disulfide nanoflower materials with a unique flower-like structure through a simple hydrothermal reaction. The preparation method is simple and efficient.

本发明通过简单的水热反应制备得到具有独特花状结构的3D二硫化钼纳米花材料，其制备方法简单高效。

To address the shortcomings of existing technologies, this invention constructs a fruit and vegetable pesticide residue degradation technology applicable to various neonicotinoid pesticides based on the prepared 3D molybdenum disulfide nanoflower material (MoS₂-CF), and elucidates the degradation mechanism.

为了解决现有技术的不足，本发明基于制备获得的3D二硫化钼纳米花材料(MoS₂-CF)构建了适用于多种新烟碱类农药的果蔬农残降解技术，并对降解机制进行阐释。

The results showed that MoS₂-CF can effectively activate persulfate (PMS), and its unique flower-like structure is conducive to the exposure of active sites and improves mass transfer efficiency.

结果表明，MoS₂-CF可有效活化过一硫酸盐(PMS)，其独特的花状结构有利于活性位点的暴露并提高传质效率。

Within 15 minutes, the degradation rates of acetamiprid, imidacloprid, and thiamethoxam residues in fruits and vegetables can reach 97.1%, 95.3%, and 100%, respectively.

15分钟内即可实现果蔬中残留啶虫脒、吡虫啉和噻虫嗪降解率达到97.1%、95.3%和100%。

At the same time, this treatment method effectively removes pesticide residues without damaging the aromatic compounds in fresh fruits and vegetables, thus ensuring their flavor and quality. It is a highly efficient and environmentally friendly new method for controlling pesticide residues in fruits and vegetables, with broad application prospects.

同时该处理方式在有效去除残留农药的同时，不会破坏新鲜果蔬本身的芳香化合物含量，确保了新鲜果蔬的风味品质，是一种高效、环保的果蔬农残控制新方法，具有广阔的应用前景。

[0037]

Attached Figure Description

附图说明

[n0034]

The accompanying drawings, which form part of this invention, are used to provide a further understanding of the invention. The illustrative embodiments of the invention and their descriptions are used to explain the invention and do not constitute an improper limitation of the invention.

构成本发明的一部分的说明书附图用来提供对本发明的进一步理解，本发明的示意性实施例及其说明用于解释本发明，并不构成对本发明的不当限定。

[n0035]

Figure 1 shows the morphology of the material prepared in Example 1 of the present invention, wherein a is a TEM image of bulk-MoS₂, b is a TEM image of MoS₂-NS, c is an HRTEM image of MoS₂-NS, d and e are TEM images of MoS₂-CF, and f is an HRTEM image of MoS₂-CF.

图1为本发明实施例1制备的材料的形貌图，其中，a为bulk-MoS₂的TEM照片，b为MoS₂-NS的TEM图，c为MoS₂-NS的HRTEM图，d和e为MoS₂-CF的TEM图，f为MoS₂-CF的HRTEM图；

[n0036]

Figure 2 shows related images of MoS₂-NS and MoS₂-CF prepared in Example 1 of the present invention, where a is the XRD spectrum, b is the XPS spectrum, c is the high-resolution XPS spectrum of Mo 3d, and d is the high-resolution XPS spectrum of S2p.

图2为本发明实施例1制备的MoS₂-NS和MoS₂-CF的相关图片，其中，a为XRD谱图，b为XPS谱图，c为Mo 3d高分辨XPS谱图，d为S2p高分辨XPS谱图；

[n0037]

Figure 3 is a data graph of the degradation of pesticide residues by MoS₂-CF prepared in Example 1 of the present invention, where a is the removal rate of three NEOs in tomatoes and b is the concentration of residual NEOs in the corresponding treated water.

图3为本发明实施例1制备的MoS₂-CF降解农残的数据图，其中，a为番茄中三种NEOs的去除率，b为对应处理水中残留NEOs的浓度；

[n0038]

Figure 4 shows the effects of different consumables on the efficiency of degradation of (a) acetamiprid, (b) imidacloprid and (c) thiamethoxam in the MoS₂-CF/PMS system, and (d) the corresponding reaction rate values; (e) EPR spectra of ¹O₂ and (f) ・OH/SO₄^{・-}.

图4为不同消耗剂对MoS₂-CF/PMS体系降解(a)啶虫脒，(b)吡虫啉和(c)噻虫嗪的效率影响及(d)相应的反应速率值；(e)¹O₂和(f)・OH/SO₄^{・-}的EPR谱图。

[0043]

Detailed Implementation

具体实施方式

[n0039]

To enable those skilled in the art to better understand the technical solution of the present invention, the technical solution of the present invention will be described in detail below with reference to specific embodiments.

为了使得本领域技术人员能够更加清楚地了解本发明的技术方案，以下将结合具体的实施例详细说明本发明的技术方案。

[n0040]

Example 1

实施例1

[n0041]

1.

1.

Experimental Section

实验部分

[n0042]

1.1 Preparation of MoS₂ series materials

1.1MoS₂系列材料制备

[n0043]

Accurately weigh 1.24 g of (NH₄)₆Mo₇O₂₄・4H₂O and 2.28 g of thiourea, disperse them in 70 mL of deionized water, stir at room temperature for 30 minutes, then transfer the solution to a 100 mL hydrothermal reactor lined with polyphenol, and react at 200 °C for 12 hours.

准确称取1.24g(NH₄)₆Mo₇O₂₄・4H₂O和2.28g硫脲，分散于70mL去离子水中，室温搅拌30分钟后，将溶液转移至100mL聚苯酚内衬的水热釜中，在200°C条件下反应12小时。

After the reaction, the product was collected by centrifugation, washed several times with deionized water and ethanol, and dried overnight in a vacuum drying oven at 60°C.

反应后，离心收集产物，并用去离子水和乙醇清洗数次，于真空干燥箱内60°C烘干过夜。

The resulting material is labeled MoS₂-CF.

所得材料标记为MoS₂-CF。

[n0044]

In addition, a liquid-phase exfoliation method was used to exfoliate commercially available bulk MoS₂(bulk-MoS₂) to obtain two-dimensional molybdenum disulfide nanosheets, which were labeled as MoS₂-NS.

此外，采用液相剥离法，剥离商品化块状MoS₂(bulk-MoS₂)，获得二维二硫化钼纳米片，该材料标记为MoS₂-NS。

[n0045]

1.2 Degradation Experiment

1.2降解实验

[n0046]

The research subjects were neonicotinoid pesticides acetamiprid (ACE), imidacloprid (IMI), and thiamethoxam (THI).

研究对象为新烟碱类农药(NEOs)啶虫脒(ACE)、吡虫啉(IMI)和噻虫嗪(THI)。

First, prepare 100 mL of a standard solution of three neonicotinoid pesticides with a concentration of 1000 mg L⁻¹ using acetonitrile.

首先，用乙腈配制100mL浓度为1000mg L⁻¹的三种新烟碱类农药标准溶液。

Then, the tomato fruit was coated with a standard solution and air-dried at room temperature (addition level: 0.5 mg L⁻¹).

然后用标准溶液涂抹番茄果实，在室温下风干(添加水平为0.5mg L⁻¹)。

Tomato samples were randomly collected after contamination, and the initial NEO residue levels were tested.

随机采集污染后的番茄样品，检测初始NEO残留量。

Then, the same number of tomatoes were placed in a 5-liter stainless steel food container containing 2 liters of water, with 0.03g L⁻¹MoS₂-CF and 0.8mM PMS (these two concentrations are the concentrations in the aqueous solution) or both added.

随后，将相同数量的西红柿放入5升不锈钢食品容器中，容器中装有2升水，其中加入0.03g L⁻¹MoS₂-CF、0.8mM PMS(上述两个浓度为水溶液中的浓度)或两者兼而有之。

The processing time is set to 15 minutes.

处理时间设定为15min。

A control experiment was conducted using pure water.

在纯净水中进行对照实验。

Each process is repeated three times.

每个过程重复三次。

[n0047]

1.3 Analytical Methods

1.3分析方法

[n0048]

The improved QuEChERS method was used to quantify pesticide residues.

采用改进QuEChERS方法定量农药残留量。

Weigh 10.0g of homogenized tomato fruit sample into a 50mL centrifuge tube.

将10.0g均质番茄果实样品称重至50mL离心管中。

Add 10 mL of acetonitrile and vortex extract for 2 min.

加入10mL乙腈，旋涡提取2min。

Then add 3g of NaCl and vortex for 2 minutes.

然后加入3g NaCl，再旋涡2分钟。

After centrifugation at 3800 rpm for 5 minutes, 6 mL of supernatant was transferred to commercially available dispersion solid phase extraction nanotubes (trade number 5982-5256, Agilent Technologies), vortexed for 2 minutes, and then centrifuged at 10000 rpm for 2 minutes.

3800rpm离心5分钟后，将6mL上清转移到商用分散固相萃取纳米管(商品号5982-5256，AgilentTechnologies)中，旋涡2分钟，然后10000rpm离心2分钟。

Take 1 ml of supernatant, filter it through a 0.22 µm nylon membrane, and transfer it to a vial for further analysis.

取1毫升上清液过0.22µm尼龙滤膜，并转移到进样小瓶中进行后续分析。

[n0049]

The concentration of the target pesticide was analyzed using ultra-high performance liquid chromatography (UPLC, Waters) and orbital trap mass spectrometry (MS, SCIEX).

利用超高效液相色谱(UPLC,Waters)和轨道阱质谱(MS,SCIEX)分析目标农药的浓度。

Gradient elution was performed using an ACQUITY UPLC BEH C18 column (1.7 µm, 2.1 mm × 100 mm, Waters).

采用ACQUITY UPLC BEH C18色谱柱(1.7µm,2.1mm×100mm,Waters)进行梯度洗脱。

The mobile phase was acetonitrile (A) and 0.1 vol% formic acid (B), and the flow rate was 0.35 mL min⁻¹.

流动相为乙腈(A)和0.1vol%甲酸(B)，流速为0.35mL min⁻¹。

The gradient elution procedure was as follows: 0 min 10% A; 1 min 10% A; 4.5 min 90% A; 5.5 min 90% A; 5.6 min 10% A; 6.5 min 10% A, with an injection volume of 2 µL.

梯度洗脱操作如下：0min 10%A；1分钟，10%A；4.5min,90%A；5.5min,90%A；5.6min,10%A；6.5min,10%A，进样量2µL。

Detection is performed in MRM(+) mode.

以MRM(+)模式进行检测。

The mass spectrometry ratios of the three neonicotinoid pesticides are shown in Table 1.

三种新烟碱类农药的质谱比见表1。

[n0050]

Table 1. Molecular structures and mass spectrometry information of three neonicotinoid pesticides

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表1三种新烟碱类农药的分子结构及质谱信息

[n0052]

Qualitative ion pairs

---

*定性离子对

[n0053]

2 Results

2结果

[n0054]

2.1 Characterization of Nanomaterials

2.1纳米材料表征

[n0055]

The microstructure of the obtained MoS₂ series materials was characterized by scanning tunneling electron microscopy (TEM).

采用扫描隧道电子显微镜(TEM)表征所得MoS₂系列材料的微观形貌。

As shown in Figure 1, the commercially available bulk-MoS_NER34 material has a tightly packed layered structure. After liquid phase exfoliation, the number of layers of the resulting MoS₂-NS is significantly reduced, and a large number of edges are exposed.

如图1所示，商品化的bulk-MoS₂材料为紧密堆积的片层结构，经过液相剥离后所得MoS₂-NS的层数明显减少，并有大量边缘暴露。

High-resolution transmission electron microscopy (HRTEM) characterization confirmed the presence of the (100) crystal plane in MoS₂-NS.

高分辨透射电镜(HRTEM)表征确认了MoS₂-NS中(100)晶面的存在。

The MoS₂-CF material exhibits a unique cornflower-like morphology, and HRTEM further confirmed the 3D structure of the MoS₂-CF material, with a significant increase in interlayer spacing.

MoS₂-CF材料呈现出独特的矢车菊花朵状形貌，HRTEM也进一步证实了3D结构的MoS₂-CF材料，层间距明显增加。

[n0056]

The XRD pattern shown in Figure 2a indicates that there are significant differences in the crystal phases of MoS₂-NS and MoS₂-CF.

图2a所示的XRD图谱表明，MoS₂-NS和MoS₂-CF的晶相存在显著差异。

(002)

The typical peak of the (002) plane is located at 14.2°, indicating that the structure of MoS₂-NS is mainly composed of the 2H phase.

面的典型峰位于14.2°，表明MoS₂-NS的结构主要由2H相组成。

However, the diffraction peak shifted to 9.0° and weakened in MoS₂-NS, indicating that the structure of MoS₂-CF changed from the 2H phase to the 1T phase and the interplanar spacing increased.

但该衍射峰在MoS₂-NS中移至9.0°且强度变弱，说明MoS₂-CF的结构从2H相转变为1T相，且面间距扩大。

According to the Bragg equation, the interlayer spacing of MoS₂-CF was calculated to be 0.982 nm, which is consistent with the HRTEM measurement (Fig. 1f).

根据Bragg方程，计算出MoS₂-CF的晶面层间距为0.982nm，与HRTEM的测量值一致(图1f)。

[n0057]

The chemical composition and surface state of the prepared MoS₂ samples were investigated using XPS.

利用XPS研究了制备所得的MoS₂样品的化学成分和表面状态。

As shown in Figure 2b, the element type of MoS₂-CF is the same as that of MoS₂-NS.

如图2b所示，MoS₂-CF的元素类型与MoS₂-NS相同。

In addition, the main Mo 3d peaks of MoS₂-NS include Mo 3d_{5/2} (229.70 eV) and Mo3d_{3/2} (232.86 eV), corresponding to the 2H phase (Fig. 2c).

此外，MoS₂-NS的主要Mo 3d峰包括Mo 3d_{5/2}(229.70eV)和Mo3d_{3/2}(232.86eV)，对应于2H相(图2c)。

In contrast, MoS₂-CF also contains Mo 3d_{5/2} and Mo 3d_{3/2} peaks of 1T phase MoS₂, with binding energies of 228.93 eV and 232.12 eV, respectively.

相比之下，MoS₂-CF中还包含有1T相MoS₂的Mo 3d_{5/2}和Mo 3d_{3/2}峰，结合能分别为228.93eV和232.12eV。

As can be seen from the S2p spectrum, the two characteristic peaks of MoS₂-NS at 162.53 and 163.69 eV can be attributed to the S2p_{3/2} and 2p_{1/2} of 2H-MoS₂.

从S2p谱图可以看出，MoS₂-NS在162.53和163.69eV处的两个特征峰可以归属于2H-MoS₂的S2p_{3/2}和2p_{1/2}。

Furthermore, the standard peaks in MoS₂-CF with binding energies of 161.71 and 163.06 eV respectively should be attributed to 1T-MoS₂, further confirming that the MoS₂-CF material has undergone a transformation from the 2H phase to the 1T phase.

此外，MoS₂-CF中结合能分别为161.71和163.06eV的标准峰应归属于1T-MoS₂，进一步证实了MoS₂-CF材料发生了由2H相向1T相的转变。

[n0058]

2.2 Pesticide residue degradation efficiency

2.2农药残留降解效率

[n0059]

Tomato fruit samples contaminated with pesticides were immersed in tap water or water containing MoS₂-CF/PMS.

将农药污染后的番茄果实样品浸入自来水或含有MoS₂-CF/PMS的水中。

Each experiment was repeated three times.

每组实验均重复三次。

Before sample analysis, all tomatoes were rinsed under tap water for 10 seconds to simulate the actual home tomato consumption process.

在样品分析前，所有西红柿都在自来水下冲洗10秒，以模拟实际的家庭番茄食用过程。

As shown in Figure 3a, in the control experiment, the removal rate of the three NEOs was only 7.8%-9.2%, indicating that only a very small amount of NEOs could be removed in a short washing time.

如图3a所示，在对照试验中，三种NEOs的去除率仅为7.8%-9.2%，说明在较短的洗涤时间内仅能去除非常少量的NEOs。

The removal rates of ACE, IMI, and THI by immersion in tap water were 44.1%, 49.8%, and 46.9%, respectively.

自来水浸泡对ACE、IMI和THI的去除率分别为44.1%、49.8%和46.9%。

With the participation of MoS₂-CF/PMS, the removal rates of ACE, IMI and THI in tomatoes increased to 97.1%, 95.3% and 100%, respectively.

而在MoS₂-CF/PMS的参与下，番茄中ACE、IMI和THI的去除率分别提高到97.1%、95.3%和100%。

As can be seen from Figure 3b, the concentrations of the three NEOs in the water are relatively high, indicating that during the water soaking process, some of the residual NEOs were transferred from the tomatoes to the treated water.

从图3b中可以看出，水中三种NEOs的浓度都比较高，说明在水浸泡过程中，部分残留的NEOs从番茄转移到了处理水中。

In contrast, treating tomatoes with MoS₂-CF/PMS can completely degrade residual NEOs, thereby reducing the possibility of secondary pollution.

相比之下，用MoS₂-CF/PMS处理番茄，可以彻底降解残留的NEOs，进而减少二次污染的可能性。

[n0060]

2.3 Evaluation of Tomato Flavor Quality

2.3番茄风味品质评价

[n0061]

After treatment with MoS₂-CF/PMS, the aroma components of tomatoes remained unchanged in both quality and quantity (Table 2).

经过MoS₂-CF/PMS处理后，番茄气味成分在质量和数量上都没有改变(表2)。

Furthermore, the odor components of the top 10 high odor activity values (OAV) were the same as those of the untreated samples, and no new volatile off-odors were found in the treated samples, indicating that the MoS₂-CF/PMS treatment effectively removed pesticide residues without negatively affecting the aroma characteristics of tomatoes.

此外，前10种高气味活度值(OAV)的气味成分与未处理样品相同，并且在处理样品中没有发现新的挥发性异味，表明MoS₂-CF/PMS处理在有效去除农药残留的同时，对番茄香气特征没有负面影响。

Quantitative data on odorants showed that only 5 out of 24 odor components exhibited significant changes in their OAV (odor efficacy). Among them, the contribution of 1-hexanol decreased by 85.28%, while the aroma potency of phenylacetaldehyde, 2-phenylethanol, β-citral, and (E,E)-2,4-decaenoal increased by 50.87%, 44.94%, 34.68%, and 19.51%, respectively.

气味剂的定量数据显示，24种气味成分中只有5种的OAV发生了显著变化，其中1-己醇的贡献下降了85.28%，而苯乙醛、2-苯乙醇、β-柠檬醛和(E,E)-2,4-十烯醛的香气效力分别增加了50.87%、44.94%、34.68%和19.51%。

However, quantitative descriptive analysis of the aroma extract showed that the decrease in 1-hexanol OAV did not cause a significant change in the intensity of the tomato "fragrance". This may be because (Z)-3-hexenal, hexanal and 1-pentene-3-1 mainly impart the tomato fragrance.

然而，香气提取物的定量描述分析结果显示，1-己醇OAV的降低并没有引起番茄“清香”强度的明显变化，这可能是由于(Z)-3-己烯醛、己醛和1-戊烯-3-1主要赋予了番茄清香。

Similarly, the increase of phenylacetaldehyde, 2-phenylethanol, β-citral and (E,E)-2,4-dodecenal OAV did not significantly change the sweetness and floral aroma intensity of the MoS₂-CF/PMS treated samples.

同样，苯乙醛、2-苯乙醇、β-柠檬醛和(E,E)-2,4-十二烯醛OAV的增加并没有显著改变MoS₂-CF/PMS处理样品的甜味和花香强度。

These results also demonstrate that there were no significant sensory differences between untreated and MoS₂-CF/PMS-treated tomato fruit samples.

这些结果也证明了未经处理和MoS₂-CF/PMS处理的番茄果实样品之间没有明显的感官差异。

[n0062]

Table 2. Identification of aroma activation in tomato fruit homogenate based on DSE-SAFE-GC-O/AEDA and OAV.

表2基于DSE-SAFE-GC-O/AEDA和OAV鉴定番茄果实匀浆中的香气活性化

[n0065]

^aIdentification of the compounds was performed by comparing theirmass spectra(MS-EI), retention indices(RI) on capillaries DB5 andDB-WAX, aswell as the odor quality during sniffing with data of reference compounds.

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^aIdentification of the compounds was performed by comparingtheirmass spectra (MS-EI),retention indices(RI)on capillaries DB5 andDB-WAX,aswell as the odor quality during sniffing with data ofreference compounds.

[n0066]

^bOdor-quality perceived at the sniffing-port.

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^bOdor-quality perceived at the sniffing-port.

[n0067]

^cRetention index.

---

^cRetention index.

[n0068]

^dFlavor dilution factor.

---

^dFlavor dilution factor.

[n0069]

^eOdor threshold in water(mg/kg)

---

^eOdor threshold in water(mg/kg)

[n0070]

^fConcentration was calculated as the mean value of twodifferentworkups,and expressed in ug/g tomato puree.

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^fConcentration was calculated as the mean value of twodifferentworkups,and expressed in ug/g tomato puree.

RSD of all duplicateswereall<15%.

RSD of all duplicateswereall<15%.

[n0071]

^gOdor activity value

---

^gOdor activity value

[n0072]

[*]Odorants were only perceived during sniffing but has no MS signal

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[*]Odorants were only perceived during sniffing but has no MS signal

[n0073]

[#]Odorants showed significant difference in untreated and MoS₂-CF /PMStreated tomato samples.

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[n0074]

Category:AKET,aliphatic ketones;AALC,aliphatic alcohols;AALD,aliphatic aldehyde;SUL, volatile sulfur compounds;NHCY,

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Category:AKET,aliphatic ketones；AALC,aliphatic alcohols；AALD,aliphatic aldehyde；SUL, volatile sulfur compounds；NHCY,

[n0075]

N-containing heterocyclics; TP, terpene and their derivatives; ARO, aromatics; EST, esters

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N-containing heterocyclics；TP,terpene and their derivatives；ARO,aromatics；EST,esters

[n0076]

2.4 Degradation Mechanism Research

2.4降解机制研究

[n0077]

The active species (ROS) in the MoS₂-CF/PMS system were identified by free radical quenching experiments.

通过自由基猝灭实验，鉴定了MoS₂-CF/PMS体系中的活性物种(ROS)。

Methanol (MeOH) is a consumable of ・OH and SO₄^{・-}.

甲醇(MeOH)为・OH和SO₄^{・-}的消耗剂。

tert-butanol (TBA), p-benzoquinone (p-BQ), and furfuryl alcohol (FFA) were selected as consumables for ・OH, O₂^{・-}, and ¹O₂, respectively.

选择叔丁醇(TBA)、对苯醌(p-BQ)和糠醇(FFA)分别作为・OH、O₂^{・-}和¹O₂的消耗剂。

As shown in Figures 4a-c, the contribution trends of each ROS to the degradation of the three NEOs are the same.

如图4a-c所示，每种ROS对三种NEOs降解的贡献趋势相同。

Specifically, the addition of FFA almost completely prevented the degradation of the three NEOs.

具体来说，FFA的加入几乎完全阻止了三种NEOs的降解。

Within 60 min, the degradation rates of ACE, IMI, and THI were 7.3%, 2.2%, and 1.7%, respectively, indicating that NER86ONER87 plays a major role in the MoSNER88-CF/PMS system.

60min内ACE、IMI和THI的降解率分别为7.3%、2.2%和1.7%，表明¹O₂在MoS₂-CF/PMS体系中起主要作用。

However, the quenching of O₂^{・-} did not significantly inhibit all three NEOs, indicating that O₂^{・-} does not participate in the degradation of NEOs.

然而，O₂^{・-}的猝灭并没有对所有三种NEOs产生显著的抑制作用，这表明O₂^{・-}不参与NEOs的降解。

After the addition of TBA, the degradation rates of ACE, IMI and THI decreased by 21.0%, 10.1% and 13.2% respectively within 60 min.

添加TBA后，60min内ACE、IMI和THI的降解率分别降低了21.0%、10.1%和13.2%。

Furthermore, when MeOH was added, the degradation rates of ACE, IMI, and THI decreased by 62.6%, 48.6%, and 58.0%, respectively, within 60 minutes.

此外，当添加MeOH时，60min内ACE、IMI和THI的降解率分别下降了62.6%、48.6%和58.0%。

The results confirmed that ・OH and SO₄^{・-} also participated in the degradation reaction.

结果证实了・OH和SO₄^{・-}也参与了降解反应。

The order of contribution of the reacting species is: ¹O₂>SO₄NER98_>・OH>O₂NER100_ (Figure 4d).

反应物种的贡献顺序为：¹O₂>SO₄^{・-}>・OH>O₂^{・-}(图4d)。

In short, both the SO₄NER102_ and ・OH-mediated radical pathways and the ¹O₂-mediated non-radical pathways contribute to the degradation of the three NEOs.

简而言之，SO₄^{・-}和・OH介导的自由基途径和¹O₂介导的非自由基途径都有助于三种NEOs的降解。

[n0078]

Electron paramagnetic resonance (EPR) spectroscopy analysis confirmed the presence of NER106ONER107 and SONER108NER109/・OH in the MoS₂-CF/PMS system.

通过电子顺磁共振光谱(EPR)分析确定了MoS₂-CF/PMS体系中存在¹O₂和SO₄^{・-}/・OH。

TEMP is a selective probe for ¹O₂, and DMPO is a selective probe for SO₄NER113_/・OH.

TEMP是对¹O₂的选择性探针，DMPO是对SO₄^{・-}/・OH的选择性探针。

In Figures 4e-f, no signals belonging to DMPO-O-NER115_^{・-}, DMPO-・OH, or TEMP-¹O₂ were observed in the absence of MoS₂-CF (0min).

在图4e-f中，在没有MoS₂-CF(0min)的情况下，没有观察到属于DMPO-O₄^{・-}、DMPO-・OH或TEMP-¹O₂的信号。

However, EPR signals can be detected in both the MoS₂-CF/PMS/DMPO and MoS₂-CF/PMS/TEMP systems.

然而，在MoS₂-CF/PMS/DMPO体系和MoS₂-CF/PMS/TEMP体系中都可以检测到EPR信号。

After adding MoS₂-CF, characteristic signals of TEMP-¹O₂(1:1:1), DMPO-SO₄NER125_(6 peaks) and DMPO-・OH(1:2:2:1) were observed.

加入MoS₂-CF后，观察到TEMP-¹O₂(1:1:1)、DMPO-SO₄^{・-}(6个峰)和DMPO-・OH(1:2:2:1)的特征信号。

Therefore, MoS₂-CF can activate PMS to generate ¹O₂, SO₄NER130_ and ・OH, which is consistent with the aforementioned results of radical capture.

因此，MoS₂-CF可以激活PMS生成¹O₂、SO₄^{・-}和・OH，这与前述自由基捕获的结果一致。

[n0079]

The above description is only a preferred embodiment of the present invention and is not intended to limit the present invention. For those skilled in the art, the present invention can have various modifications and variations.

以上所述仅为本发明的优选实施例而已，并不用于限制本发明，对于本领域的技术人员来说，本发明可以有各种更改和变化。

Any modifications, equivalent substitutions, improvements, etc., made within the spirit and principles of this invention shall be included within the scope of protection of this invention.

凡在本发明的精神和原则之内，所作的任何修改、等同替换、改进等，均应包含在本发明的保护范围之内。