

Electronic Supporting Information

Ingestion and Insecticidal Effects of Cetylpyridinium Chloride Functionalized Carbon Nanotubes on *Spodoptera litura*: Oxidative Stress, Metabolic Disruptions, and Reproductive Toxicity

Mohd Jameel¹, Fouzia Mashkoor², Mohd Amir³, Mohd Shoeb^{2*}, Changyoon Jeong^{2*}

¹ Department of Zoology, Aligarh Muslim University, Aligarh, 202002, Uttar Pradesh, India

²School of Mechanical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, 38541, Republic of Korea

³Department of Biochemistry, Faculty of Life Sciences, Aligarh Muslim University Aligarh, 202002, Uttar Pradesh, India

Corresponding Author(s)

Dr. Changyoon Jeong²

Email: yoonni22@yu.ac.kr

Dr. Mohd Shoeb²

Email: shobynasa@gmail.com; mshoeb@yu.ac.kr

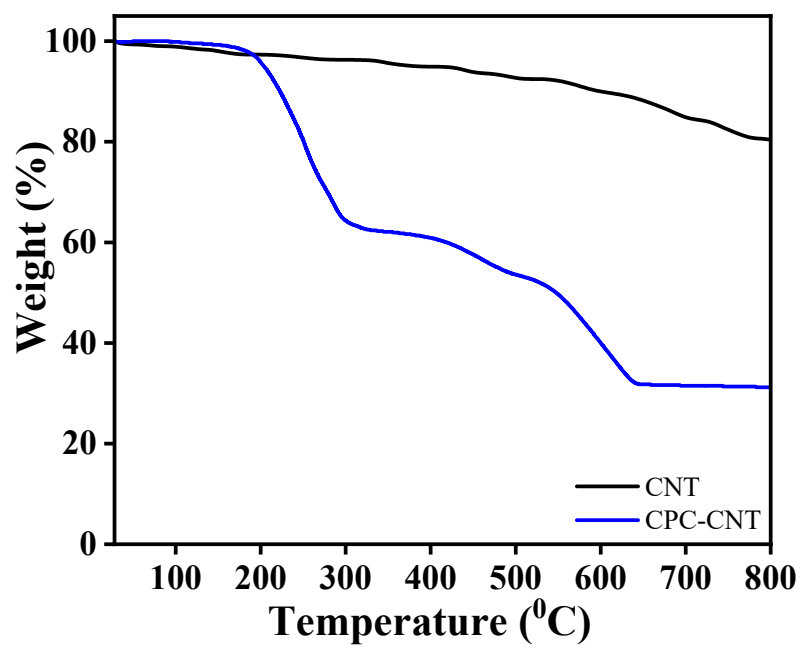


Figure S1. TGA analysis of CNT and CPC-CNT.

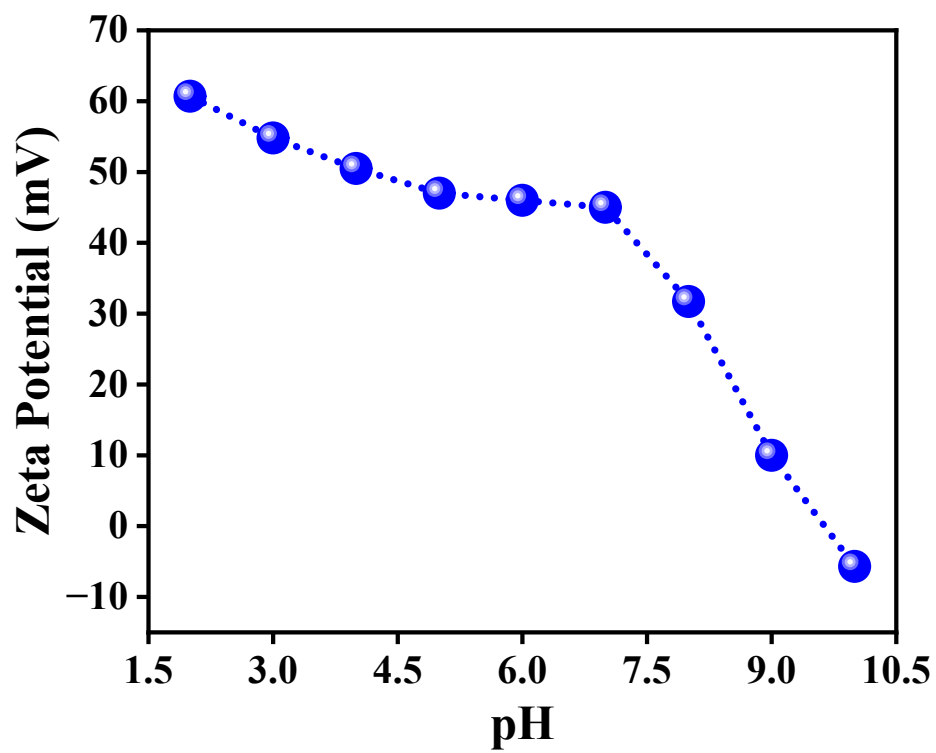


Figure S2. pH-Dependent Zeta Potential of CPC-CNT

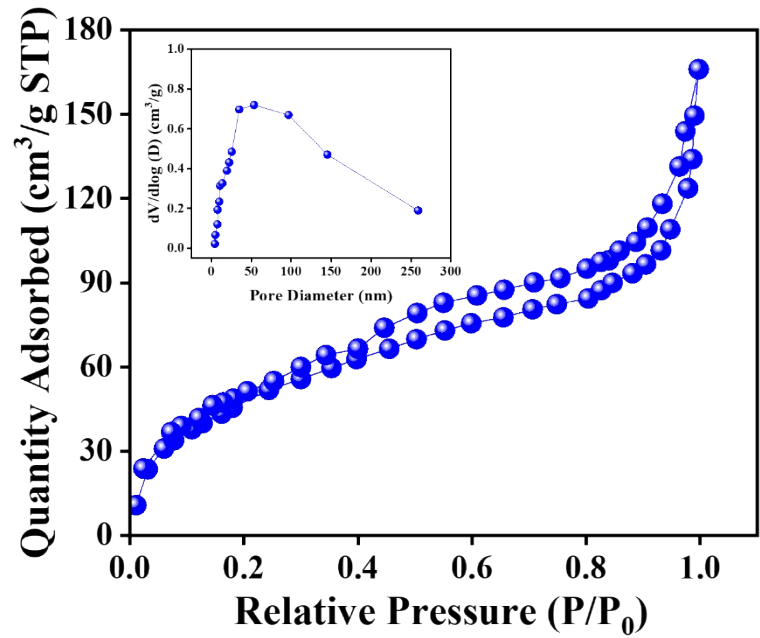


Figure S3. BET specific surface area and inset pore diameter distribution for CNT-CPC

Table S1. Comparative Overview of Nanopesticide Systems Targeting *Spodoptera litura*: Physicochemical Characteristics, Biological Effects, and Environmental Considerations

Nanopesticide Type	Source Material	Average Size (nm)	Target Organism	LC50 (g/L)	Max Mortality (%)	Effect on Development and Physiology	Environmental Considerations	Reference
Chitosan-Selenium Nanocomposite (Ch-SeNPs)	Mycosynthesized using <i>Penicillium griseofulvum</i> (fungal filtrate)	67.41	<i>Spodoptera littoralis</i>	Low LC50 (exact value not specified)	Higher than SeNPs and fungal spores	Strong larvicidal and pupicidal activity; cytotoxic ultrastructural impact; safe to honeybees	Eco-friendly biosynthesis; safe for non-target organisms (e.g., honeybees)	[1]

						es		
Selenium Nanoparticles (SeNPs)	Mycosynthesized using <i>Penicillium griseofulvum</i> (fungal filtrate)	91.25	<i>Spodoptera littoralis</i>	Low LC50 (exact value not specified)	High mortality, lower than Ch-SeNPs	Significant insecticidal activity and ultrastructural disruption in larvae	Eco-friendly biosynthesis; cost-effective; safe for pollinators	[1]
Silver Nanoparticles (AgNPs)	Chemically synthesized AgNPs	50–60	<i>Spodoptera littoralis</i>	Not applicable (nonlethal)	Not applicable	Reduced larval and pupal weight; increased plasmacyte count; no change in nutrient levels	Studied at nonlethal dose; possible immune modulation; lower metabolic interference	[2]
Zinc Oxide Nanoparticles (ZnONPs)	Chemically synthesized ZnONPs	10–30	<i>Spodoptera littoralis</i>	Not applicable (nonlethal)	Not applicable	Extended larval period; reduced weight; decreased protein, lipid, carbohydrate levels; increased hemocyte counts; enhanced amylase, G6PD, lipase, catalase, and SOD	Nonlethal dose showed significant effects on development, metabolism, and immunity	[2]

						activities		
Hydrophobic Silica Nanoparticles (TSiNP HPHO)	Tetraethyl orthosilicate (TEOS)	Not specified (very small)	Spodoptera littoralis	10.048	100%	High impact on protein, chitinase, phenol oxidase; reduced protease, amylase	Low-cost, eco-friendly	[3]
Silica Nanoparticles from Sodium Silicate (SSiNP HPHI)	Sodium silicate	Not specified (medium)	Spodoptera littoralis	10.076	100%	Same as above	Eco-friendly; low-cost from industrial byproducts	[3]
Hydrophilic Silica Nanoparticles from TEOS (TSiNP HPHI)	Tetraethyl orthosilicate (TEOS)	Not specified (big)	Spodoptera littoralis	10.401	100%	Same as above	Biocompatible, safe; expensive precursor	[3]
Microsilica from Sand (TSi)	Sand (Top-down method)	175,000 (μm size)	Spodoptera littoralis	40.299	70%	Mild effects	Low impact; low efficacy	[3]
Tungsten Oxide (WRT)	WO ₃ nanomaterial	Not specified	Spodoptera littoralis	No toxicity alone	No mortality alone	No toxic effect alone; combined increased developmental delay	Low toxicity but no standalone pesticidal effect	[4]
Magnetic Nanoparticles (MNPs)	Fe ₃ O ₄ -based magnetic nanoparticles	Not specified	Spodoptera littoralis	No toxicity alone	No mortality alone	Antagonistic in mixture; increased malform	Safe alone; activity depends on	[4]

						ations	combina tion	
Cu-Doped MNPs (MNP-Cu)	Fe ₃ O ₄ doped with Cu	Not specified	Spodoptera littoralis	No toxicity alone	No mortality alone	Induced enzyme activity (GST, α -esterase); repellent	Safe alone; combination causes stress and immune modulation	[4]
Cyromazine + MNP-Cu (500 mg/L)	Synthetic + Cu-doped magnetic nanomaterials	Not specified	Spodoptera littoralis	Not specified (repellency and enzyme effects)	No adult emergence at 500 mg/L	Max repellency (57.6%); strong immune response via Q-PCR	Promising for reduced chemical pesticide use; mixture efficiency	[4]
Cyromazine + WRT (500 mg/L)	Synthetic + WO ₃ nanomaterial	Not specified	Spodoptera littoralis	Not specified	27.3% adult emergence	Some adult emergence and moderate developmental delay	Moderate impact with adult emergence; less effective than MNP-Cu	[4]
Cu-Doped Zinc Oxide Nanoparticles (Cu-ZnONPs)	ZnO nanoparticles doped with copper (Cu) using wet chemical synthesis	Not explicitly stated; characterized via SEM and TEM	Spodoptera littoralis	Not specified; dose in % (1–5%)	95% population reduction at 5% Cu-ZnONPs after 16 days	Significant pest population reduction; strong dose-dependent toxicity; highest efficacy at 5% concentration	Eco-friendly and cost-effective; potential to reduce use of conventional insecticides and related	[5]

							risks	
Iron Nanoparticles (FeNPs)	Trigonella foenum-graecum leaf extract	Not specified (green synthesized, characterized)	S. litura, H. armigera	Not specified individually	Approx. 70–80% at 72 h	Strong antifeedant activity (up to 90–95%); suppressed detox enzymes (CarE, GST, P450); altered esterase banding	Green synthesis, plant-derived, eco-friendly	[6]
FeNPs + Fenvalerate (Fen)	FeNPs from fenugreek + synthetic pyrethroid (Fenvalerate)	Not applicable (mixture)	S. litura, H. armigera	130.31 mg/L (S. litura), 89.32 mg/L (H. armigera)	92.83 % (S. litura), 91.41 % (H. armigera) at 72 h	Synergistic toxicity; reduced detoxification enzyme activity; enhanced antifeedant response; resistance management potential	Combines lower dose synthetic pesticide with plant-based nanomaterial for reduced environmental risk	[6]
Silver Nanoparticles (AgNPs)	Green synthesis using Leonotis nepetifolia leaf extract	Not explicitly mentioned; characterized via SEM, TEM, DLS	Spodoptera litura, Helicoverpa armigera, Aedes aegypti, Culex quinquefasciatus	47.44 ppm (Aedes aegypti), 35.48 ppm (Culex quinquefasciatus)	Larval mortality: 78.49 % (S. litura), 72.70 % (H. armigera); Pupal mortality	Antifeedant activity: 78.77% (S. litura), 82.16% (H. armigera); Histological	Eco-friendly biosynthesis; high efficacy; potential to reduce chemical insecticide use;	[7]

					ty: 84.66 % (S. litura), 77.44 % (H. armige ra)	damage to epithelial and goblet cells in larval midgut	suitable for agricultu ral and public health applicati ons	
CSNp- BV (Chitosa n NPs with Beauver icin)	Chitosan + Beauveri cin (from Beauveri a bassiana)	160– 230	Spodopt era litura	Not specified, dose- dependen t response observed	100% (early instars)	Reduced pupal and adult emergen ce, dose- depende nt mortality in all larval stages	Biocom patible, controlle d release, environ mentally friendly formulat ion	[8]
CdS	Cadmiu m acetate & thiourea via CTAB- based method	60	Spodopt era litura	0.50884	93.79	Disruptio n of midgut epithelial cells, stiffenin g, oozing of body contents, prematur e moulting	Toxicity due to cadmiu m, possible ecologic al impact	[9]
Nano- Ag	Acid leaching tail solution and hydrazini um sulphate reduction	<90	Spodopt era litura	1.40314	56.89	Disruptio n of digestive system, oozing of gut content, cell damage	Toxic to aquatic systems, can cause chromos omal aberratio ns	[9]
Nano- TiO2	Anatase with amines and NaOH	>50	Spodopt era litura	0.79110	73.79	Midgut rupture, larval swelling, discharg e of	Toxicity depends on particle size and exposure	[9]

						contents, stiffened body	; less data available	
Selenium Nanoparticles (SeNPs)	Mycosynthesized using <i>Trichoderma</i> sp. culture filtrate	40–100	<i>Spodoptera litura</i>	39.739 ppm	Significant larval mortality at 48 h (LC90 = 142.839 ppm)	Strong larvicidal and antifeedant activity; histopathological damage; spherical crystalline SeNPs confirmed	Biogenic synthesis; fungal-mediated; potentially eco-friendly alternative to chemical insecticides	[10]
Fe0 Nanoparticles (Fe0NPs) from <i>Beauveria brongniartii</i>	Mycosynthesized using <i>Beauveria brongniartii</i> conidia	410–800 nm (0.41–0.80 µm)	<i>Spodoptera litura</i>	59 ppm (7 days post-treatment)	Not stated directly; increased mortality with dose and time	Reductions in feeding, growth rate, enzyme activity (GST, antioxidants); altered nutrient utilization	Fungus-mediated biosynthesis; supports eco-friendly pest control	[11]
Silver Nitrate Nanoparticles (AgNPs)	<i>Cymbopogon citratus</i> extract with AgNO ₃	Not specified in summary	<i>Spodoptera litura</i>	Not mentioned	98% (AgNPs with <i>C. citratus</i> , ethanol-based)	Prolonged larval toxicity; high mortality at 72 h post-exposure	Eco-friendly biosynthesis, ethanol as non-toxic dispersant	[12]
Zinc Oxide Nanoparticles (ZnONPs)	Various plant extracts with ZnO	Not specified in summary	<i>Spodoptera litura</i>	Not mentioned	90% (ZnONPs with ethanol)	Larval mortality; ethanol improves dispersion and	Sustainable alternative to chemical insecticides	[12]

						toxicity	des	
Copper Nanoparticles (CuNPs)	Copper salt precursor	N/A	Spodoptera litura	N/A	74.44 (leaf dip), 68.89 (larval dip)	Dose-dependent larval mortality observed ; effective by both leaf and larval dip methods	Potential eco-friendly alternative to synthetic insecticides	[13]
CPC-function alized Carbon Nanotubes (CPC-CNTs)	Carbon nanotubes functionalized with cetylpyridinium chloride (CPC)	~30–50	Spodoptera litura	~0.68% (estimated)	42.20 % at 0.6% concentration	↑ MDA (oxidative stress), ↓ SOD/CAT, ↓ AChE (neurotoxicity), ↓ fecundity, ↓ fertility, ↓ adult emergence	Potential concern due to CNT persistence; CPC is a cationic surfactant—eco-safe handling required	This study

References

- [1] S.A. Ibrahim, F.M. Reda, E.M. Abd-ElAzeem, M.S. Hashem, H.A. Ammar, Mycosynthesis of chitosan-selenium nanocomposite and its activity as an insecticide against the cotton leafworm *Spodoptera littoralis*, *Scientific Reports*, 15 (2025) 1012.
- [2] A.M.A. Ibrahim, A.M. Ali, Silver and zinc oxide nanoparticles induce developmental and physiological changes in the larval and pupal stages of *Spodoptera littoralis* (Lepidoptera: Noctuidae), *Journal of Asia-Pacific Entomology*, 21 (2018) 1373-1378.
- [3] M. Hashem, M. Sabbour, S. Ahmed, E.A. Abd, A. Montaser, K. Mohamed, Efficacy of silica nanoparticles on cotton leaf worm larvae, *Spodoptera littoralis* (Bosid.) (Lepidoptera: Noctuidae), *Plant Archives*, 19 (2019) 2601–2607.

- [4] S. Eldesouky, D. Aseel, M. Elnouby, E. Hafez, A. Al-Fargah, H. Hussein, Tungsten oxide, magnetic and Cu-doped magnetic nanoparticles mixtures with cyromazine as promising eco-friendly strategies to control of *Spodoptera littoralis* (Boisd.) (Lepidoptera: Noctuidae), 2023.
- [5] E.A. Abd El-Latef, M.N. Wahba, S. Mousa, G.T. El-Bassyouni, A.M. El-Shamy, Cu-doped ZnO-nanoparticles as a novel eco-friendly insecticide for controlling *Spodoptera littoralis*, *Biocatalysis and Agricultural Biotechnology*, 52 (2023) 102823.
- [6] R. Muthusamy, G. Ramkumar, S. Kumarasamy, N.T.L. Chi, S. Al Obaid, S. Alfarraj, I. Karuppusamy, Synergism and toxicity of iron nanoparticles derived from *Trigonella foenum-graecum* against pyrethroid treatment in *S. litura* and *H. armigera* (Lepidoptera: Noctuidae), *Environmental Research*, 231 (2023) 116079.
- [7] T. Manimegalai, K. Raguvanan, M. Kalpana, R. Maheswaran, Green synthesis of silver nanoparticle using *Leonotis nepetifolia* and their toxicity against vector mosquitoes of *Aedes aegypti* and *Culex quinquefasciatus* and agricultural pests of *Spodoptera litura* and *Helicoverpa armigera*, *Environmental Science and Pollution Research*, 27 (2020) 43103-43116.
- [8] S. Karthick Raja Namasivayam, A.B. R S, S.S. Shankar, Biocompatible Chitosan Nanoparticles Incorporated Pesticidal Protein Beauvericin (Csnp-Bv) Preparation for the Improved Pesticidal Activity Against Major Groundnut Defoliator *Spodoptera Litura* (Fab.) (Lepidoptera; Noctuidae), 2014.
- [9] A. Chakravarthy, C. Muniyappa, S. Kandakoor, A. Bhattacharya, K. Dhanabala, K. Gurunatha, P. Ramesh, Bio efficacy of inorganic nanoparticles CdS, Nano-Ag and Nano-TiO₂ against *Spodoptera litura* (Fabricius) (Lepidoptera: Noctuidae), *Curr. Biot.*, 6 (2012).
- [10] M. Arunthirumeni, V. Veerammal, M.S. Shivakumar, Biocontrol Efficacy of Mycosynthesized Selenium Nanoparticle Using *Trichoderma* sp. on Insect Pest *Spodoptera litura*, *Journal of Cluster Science*, 33 (2022) 1645-1653.
- [11] J. Xu, K. Zhang, A.G.S. Cuthbertson, C. Du, S. Ali, Toxicity and Biological Effects of *Beauveria brongniartii* Fe₀ Nanoparticles against *Spodoptera litura* (Fabricius), *Insects*, 11 (2020) 895.
- [12] A. Shabir, Z.M. Sarwar, H. Ali, Eco-friendly approaches of zinc oxide and silver nitrate nanoparticles along with plant extracts against *Spodoptera litura* (Fabricius) under laboratory conditions, *Sci Prog*, 106 (2023) 368504231219171.
- [13] S. Arti, M. P, P. P, S. V, U. D, I. S, Efficacy of copper nanoparticles on larval mortality of *Spodoptera litura*, *International Journal of Advanced Biochemistry Research*, 8 (2024) 286-289.