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REVIEW ARTICLE

High potential of biosynthesized nanoparticles as an efficient and inexpensive tool for SERS-detection of explosives based on trinitrotoluene

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Abstract. This review is focused on overcoming the consequences of the ruscist invasion in Ukraine and exploring solutions to the problem of contamination by explosives, such as 2,4,6-trinitrotoluene (TNT). Recognizing the need to protect the civilian and military population, it is most important to develop a simple, rapid, and sensitive detection method that first responders can use in the field to identify the TNT threats to the environment or human safety. Surface-enhanced Raman spectroscopy (SERS) is regarded as a novel detection method with high sensitivity, high specificity, and rapid response, which has been successfully applied to the biochemical detection of toxic analytes or environmental pollutants. Green, in particular plant- and fungi-mediated, synthesized metallic nanoparticles are capable of enhancing the SERS signal from various substances, with the ability to register a SERS spectrum from a single target molecule. In general, the method for plant- and fungi-based nanoparticles fabrication is as follows. First, parts of plant or fungal material are selected and crushed to obtain the extract which is processed to remove any impurities. The precursor, typically a metallic solution, is then mixed with the obtained extract, resulting in the production of nanoparticles. Maintaining appropriate pH, temperature, and continuous stirring,which ensures the production of uniformly sized nanoparticles, is crucial to facilitate the reaction effectively. The combination of affordable and sustainable production and high analytical capabilities makes this sort of nanostructure a promising candidate for investigations and decontamination of large territories of Ukraine affected by explosive compounds and products of their decay.

Keywords: green synthesis, localized plasmon resonance, metallic nanoparticles, SERS substrate, trinitrotoluene detection

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The progress of methods for sighting explosives based on Surface-Enhanced Raman Spectroscopy (SERS) is of primary importance from the viewpoint of countering potential threats in the field of national and global security. SERS stands out as a highly promising method for ultra-sensitive chemical analysis of both organic and inorganic substances, bringing it closer to practical utilization (Mazur et al., 2025). According to the Interpol review (Klapec et al., 2023), the analysis and detection of explosives and explosive residues using SERS technology can be adaptable to the current approaches to explosives analysis and will be useful in future real-world applications.

Explosives are widely applied as the explosive charges in artillery pieces and aerial bombs used in military activities, as well as in scientific and technological practice, such as mining and engineering blasting. Incorrect techniques in the manufacturing and use of explosives may be the reason for the pollution of the environment in some areas. Among the various explosives-based nitroaromatic compounds, trinitrotoluene (TNT), cyclotrimethylene-trinitroamine (RDX), and cyclotetramethylene-tetranitramine (HMX) are the most military-used environmental pollutants (Yang et al., 2021).

TNT as the substance successively synthesized by the nitration of toluene was used in weaponry during World War I in 1914–1918 as it is preferred over dynamite since the shock waves produced by TNT can penetrate the steel on armor-plated military transport. During World War II, two new explosives based on toluene were introduced, RDX and PETN (pentaerythrito-tetranitrate). RDX was renamed as Composition-4 or C-4 explosive (Awasthi et al., 2022).

The TNT is the most widespread explosive used by industries, militaries, and terrorists. TNT is widely used in landmines and underwater imploding works, resulting in soil and groundwater contamination. Purification of soil and wastewater from TNT contamination is always difficult and rather expensive (Jamil et al., 2015).

Classified as a Class C carcinogen by the Environmental Protection Agency (USA), TNT exhibits a toxic effect on all tested living organisms: in animals causing hepatitis, cataracts, anemia, skin irritation, and bone marrow hyperplasia; in soil seriously affecting the microbial diversity and vegetation. In plants, most of TNT remains in the root tissues, where growth and development are inhibited, reducing the total biomass (Johnston et al., 2015).

TNT is classified as a worldwide pollutant at concentrations above 2 μg L^{-1} (8.8 nM), contaminating manufacturing waste sites, industrial mines, current and former conflict zones, and military lands (Alizadeh, Yoosefian, 2023). TNT can penetrate human skin and enter the bloodstream, furthermore, as residual TNT in water and soil generally exists at very low concentrations, it must be detected at trace levels to safeguard human health and prevent the environmental pollution (Gao et al., 2022). In order to protect the civilian and military population, it is most important to develop an identification procedure that should be simple, rapid, and sensitive, and which can be applied by first responders in the field for the identification of TNT threats, whether to the environment, or human safety (Jamil et al., 2015).

A variety of techniques are presently approachable for the TNT assay in water and soil samples (To et al., 2020). These methods involve infrared and luminescence spectroscopy (Banas et al., 2023; Li et al., 2023), ion mobility spectrometry (Li et al., 2022), neutron activation analysis (Silarski, Nowakowski, 2022), immunoassays (Devi et al., 2022), electrochemistry (Apak et al., 2023), and molecularly imprinted polymers (Karadurmus et al., 2022). Also currently, TNT can be detected by mass spectrometry (Son, Choi, 2023), electrospray droplet impact/secondary ion mass spectrometry (Hiraoka et al., 2023), gas chromatography (Xu et al., 2023), colorimetry (Junaid et al., 2022), fluorescent polymers (Bener et al., 2022), and sensors based on plasmon resonance (Chegel et al., 2020).

However, most of these methods are expensive, non-portable, and potentially limited by extensive sample preparation. For example, mass spectrometry needs isolation and purification of the analytic probe, usually by chromatography. In addition, the sensitivity, selectivity, reproducibility, operability, and time cost of these techniques are inappropriate for trace detection of TNT. In contrast, Surface-Enhanced Raman Spectroscopy (SERS) is a novel detection method with high sensitivity, high specificity, and rapid response, which has been successfully applied to biochemical detection of toxic analytes or environmental pollutants (Xu et al., 2017, 2022).

As a physical phenomenon, SERS is the vibrational Raman scattering from molecules or inorganic nanostructures placed in the nm-vicinity of a noble metal nanostructure that strongly concentrates the electric field of the laser light and thus enhances the Raman scattering from the vibrations of molecular bonds in this spatial area. Such a strong local electric field can be created by these types of nanostructured metal because the laser can excite in them strong oscillations of free electron charges, that is called Localized Surface Plasmon Resonance (LSPR). By varying the composition (e.g., Ag, Au, or their alloy), size, and shape of metal nanostructures, the spectral position of LSPR can be tuned over the whole visible and near-infrared range (Demydov et al., 2021), while using semiconductors (Llorente et al., 2017) or some doped oxides allow shifting the LSPR deeper into the IR. Such a spectral tunability of the LSPR, and thus the SERS, allows a resonant detection of certain analytes, employment of the transparency windows of bio-tissues, avoiding fluorescent background, and other benefits. The plasmonic nanostructures capable of the aforementioned enhancement of the Raman signal are generally referred to as "SERS-substrates", even if they are in the form of colloidal nanoparticles (NPs).

Being based on Raman spectroscopy, SERS is thus well known for different toxicant analyses with high specificity — able to provide unique fingerprint-alike data, high sensitivity — possible of single molecules identification, rapid detection, and portability. One of the keys to getting higher sensitivity in a SERS assay is to effectively bring the analyte (target molecule) within the nm-range distance from the surface of the SERS substrate. In particular, it can be achieved by removing the stabilizing molecules around the colloidal NPs (Stefancu et al., 2018) or using additional ions to couple the analyte to the enhancing metal surface electrostatically (Hu et al., 2023).

When the analyte molecule is in direct contact with the metal surface, in addition to the "plasmonic" enhancement described above, the "chemical" enhancement of the Raman signal takes place due to the change in polarization of the studied molecules *via* electronic interaction with a metal (Graham et al., 2017). The latter gives rise to a modification in the electronic structure of molecules, and this modification can manifest itself both in the shift of electron levels and in the emergence of new ones. Because of the resonance Raman scattering between 'new' electron levels, the selective enhancement of separate vibrational bands occurs (Dzhagan et al., 2022a).

The research on the detection and identification of explosives by SERS began through the analysis of TNT in 1995 (Kneipp et al., 1995), and expanded later to many other explosives (Rozo et al., 2007; Gong et al., 2014; Zapata et al., 2016; Chio et al., 2019; Gao et al., 2020). The exciting sensitivity of the SERS method has already been reported — down to 10^{-17} M for TNT and 10^{-13} M for less intensively investigated but also often used explosives (Zapata et al., 2016).

It has been found that even relatively facile routes of obtaining plasmonic NPs by chemical reduction in aqueous solution enable decent levels of TNT detection, ~10^{-10} M. However, this seemed to be efficient in the solution, because of a pronounced dependence of the SERS intensity on pH. Thus the aforementioned low concentration, ~10^{-10} M, was registered only at pH = 13, while at pH = 12 the intensity dropped significantly and no Raman peaks were observed at lower pH (Rozo et al., 2007).

Although facile colloidally synthesized NPs were often applied to TNT detection as mentioned above, most of the works used more sophisticated approaches to reach high sensitivity of detection. Among the reported, there is a novel highly ordered nano-micro hierarchical structure on a flexible polydimethylsiloxane (PDMS) layer as a SERS stamp for ultrasensitive detection, which can generate high SERS signals with silver nanoparticles (AgNPs) owing to a multiscale coupling electromagnetic enhancement mechanism (Gao et al., 2020). Note, however, that, compared to the impressive detection limit of 10^{-13} mol/L achieved for a solution dropped on the substrate, the practical application proceeded by wiping the cloth bag resulted in the detection of the TNT residues with an expectedly much lower limit of 10^{-9} mol/L (Gao et al., 2020).

The reproducibility and selectivity of SERS sensors for nitroaromatics can be significantly improved *via* a hierarchical host-guest self-assembly approach mediated by the multifunctional macrocyclic molecule cucurbit[7]uril (CB[7]) (Chio et al., 2019).

Irrespective of a level of complexity/simplicity of the SERS substrate design and fabrication procedure, the free-standing NPs produced by colloidal synthesis can be an essential component in most cases. The reason is that in many real-life situations, sampling needs to be performed from a solid surface and thus requires the SERS-substrate in the form of an elastic polymer or cotton swab (Gong et al., 2014; Liu et al., 2020).

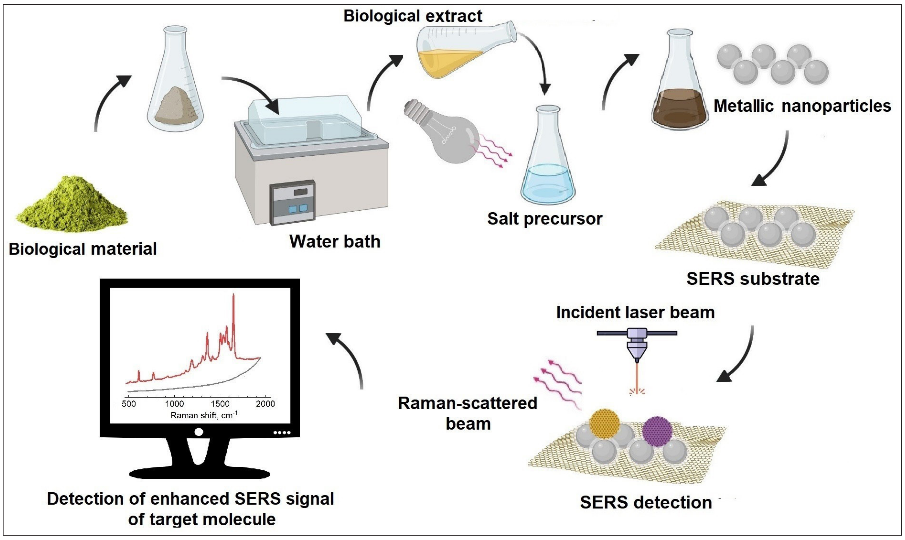

Fig. 1. Schematic illustration of the green synthesis of Ag, ZnO, and Ag/ZnO nanoparticles and its application as SERS substrate

Presently, NPs are characteristically synthesized by physical and chemical methods, which are usually costly and environmentally hazardous. That is why, the eco-safety biosynthesis also known as a green synthesis of NPs has attracted increasing attention in the last decade, in parallel with the increased interest in green chemistry approaches and environmental sustainability (Borovaya et al., 2021; Pandit et al., 2022). Traditional physical and chemical methods used for the synthesis of NPs frequently require scrupulous observance of strict conditions, whereas green synthesis routes involve simple, nontoxic, and eco-friendly protocols at an ambient temperature and pressure (Alharbi et al., 2022).

Modern eco-friendly protocols of NPs fabrication enclose the recent developments in the formulation of plant-mediated and fungal-mediated nanocomposites by using several plant and fungal species and the impact of secondary metabolites on their biocompatible functioning. Phyto (myco)-synthesis produces diverse nanomaterials with biocompatibility, environment-friendliness, and *in vivo* actions, characterized by varying sizes, shapes, and biochemical nature. This process is advantageous to conventional physical and chemical procedures. Diverse plant and fungal species are widely utilized to produce NPs as they form eco-friendly bio-factories capable of converting metal ions into their zerovalent or nanoforms. A variety of secondary metabolites, enzymes, and proteins present in plant sources act as reducing agents in this process (Malik et al., 2025; Meera et al., 2025).

We earlier reported on green synthesis and successful use as an SERS substrate of Ag, ZnO, and Ag/ZnO NPs as summarized in Fig. 1 (Smirnov et al., 2023a).

The based on noble metal NPs with LSPR that can amplify Raman scattering from the analyte are commonly referred to as "SERS substrates". Raman spectroscopy serves as a highly efficient and non-invasive method for the velocity investigation of various materials by investigation of their vibrational spectra. The role of SERS is to enhance weak Raman signals. In contrast to conventional Raman spectroscopy, SERS enables the detection of molecules even in minute concentrations in solutions or when deposited onto nanostructured noble metal films (Langer et al., 2019).

The basis for the synthesis of stable colloidal solutions of NPs were extracts of pericarps of *Capsicum annuum* L. (Dzhagan et al., 2022b), rhizomes and inflorescences of *Lathraea squamaria* L. (Smirnov et al., 2022), and fruiting bodies of *Ganoderma lucidum* (Curtis) P. Karst. (Dzhagan et al., 2023; Smirnov et al., 2023a, 2023b).

Green synthesis techniques are based on the biogenic reduction of metal precursors to produce corresponding NPs (Fig. 2). This route makes use of natural resources, often production waste and bioactive molecules, that can act as reducing, capping, and

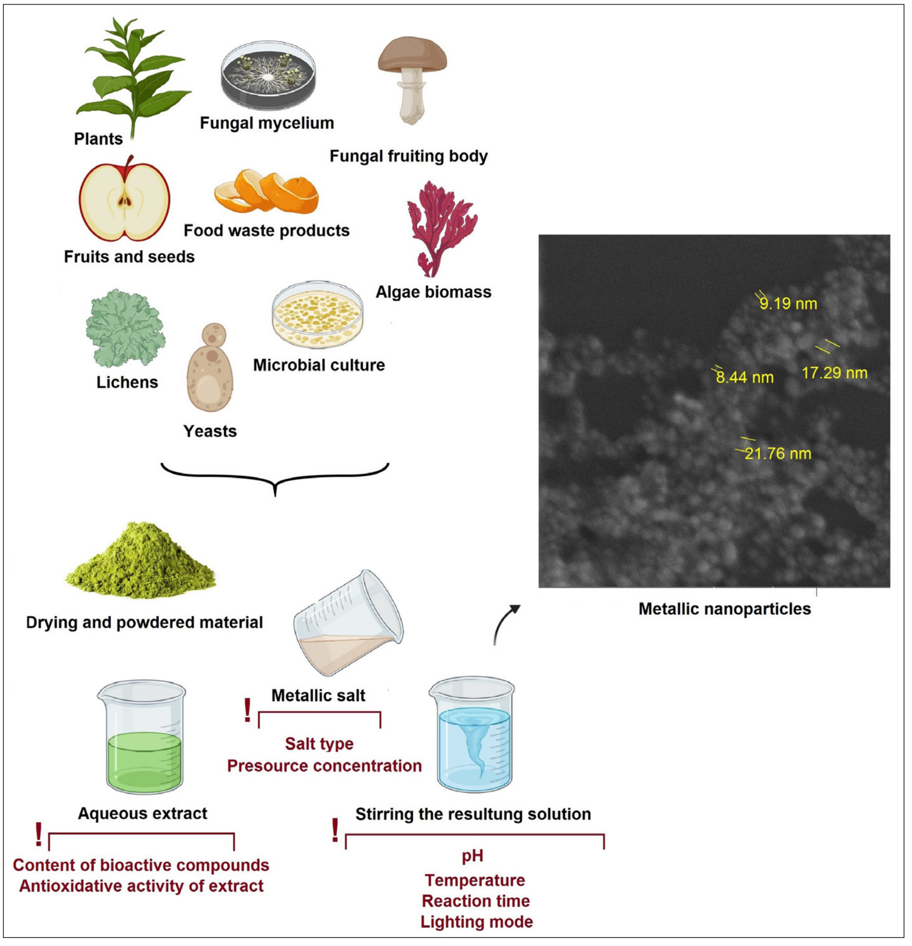

Fig. 2. Schematic diagram of the green synthesis route of metallic nanoparticles

stabilizing components in the facile synthesis of nanoparticles. Green synthesis offers numerous advantages, including the development of processes with minimal environmental impact and improved safety for nanoparticle synthesis. Overall, the synthesis of nanoparticles using green chemistry is a promising approach for sustainable and efficient production (Álvarez-Chimal, Arenas-Alatorre, 2023).

Using plant resources, the green synthesis of nanoparticles is inexpensive, faster, and considered a facile synthesis while canning or even improving the physical and chemical properties of the nanoparticles. With the great potential of this method and the sustainable and efficient production of nanoparticles, different morphology can be synthesized, which makes it a very attractive option not only for the synthesis of nanoparticles but also for the application of this method in the synthesis of other compounds.

They are environment-friendly, less expensive, and free of chemical contaminants for medical and biological applications where the purity of NPs is of main concern. Biogenic reduction is a "Bottom Up" approach similar to chemical reduction where a reducing agent is replaced by an extract of natural products (various parts of plants, fungi, yeasts, microbial cultures) with inherent stabilizing, growth terminating, and capping properties. Furthermore, the nature of biological entities in different concentrations in combination with reducing and capping organic agents influences the size and morphology of green synthesized NPs (Abdelmigid et al., 2022; Habeeb et al., 2022).

The features used for green synthesis, such as temperature, pH, the specification of precursor salts, concentration of the extract, and incubation (reaction) period, have great effects on the formation

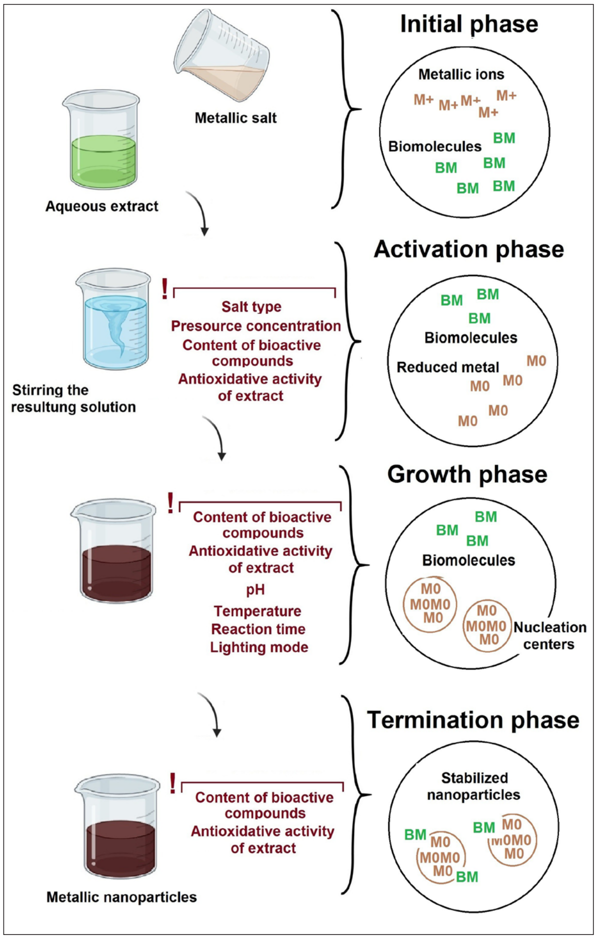

Fig. 3. Schematic diagram of the phases involved in the biosynthesis (green synthesis) of nanoparticles

and characteristics of NPs green synthesis (Fig. 3). Among these parameters, the temperature, pH value, and biological extract play a dominant role in the eco-friendly fabrication of metallic NPs (Fagier et al., 2021; Alharbi et al., 2022).

Temperature is one of the most considerable features that affect the size and shape of green synthesized NPs. Previous investigations have revealed that the dimensions of metallic NPs decrease as the temperature of green synthesis increases, resulting in a change in their shape. Hence, in NPs fabrication, it is well established that high temperatures promote nucleation, whereas low temperatures promote growth processes (Ying et al., 2022).

Numerous research publications do not mention the pH effect in the green synthesis of NPs. Nevertheless, a pH value has a vital role in the synthesis route and characteristics of NPs (Samuel et al., 2022). Phytochemicals and other natural compounds existing in a biological extract are highly linked to the pH changes and consequently to a charge change in the solution, which might change their reducing and capping properties and then NPs nucleation and growth. In conformity with this, pH can affect the morphology and productivity of the green synthesis of NPs (Elsayed et al., 2022).

Previously, we investigated the effects of pH (2.5; 5; 7; 9, and 11) on the green synthesis of AgNPs using the fruiting bodies of *Ganoderma lucidum*. Stable NPs colloids with distinct plasmonic resonance peaked at 408–418 nm are obtained by using photoreduction in a broad pH range (5 to 11). The synthesis efficiency drops only at very acidic conditions, pH = 2.5 (Smirnov et al., 2023).

In total, optimal pH for green synthesis of NPs depends on a substrate and contents of phytochemical molecules as reducing and capping agents to synthesize nanoparticles. However, Mata et al. (2009) indicated clearly that higher pH favored a higher reducing power for the green synthesis of plasmonic NPs. Notably, the high pH values were shown to be required for efficient SERS detection of TNT (Rozo et al., 2007).

The biological extract plays the main role in NPs green synthesis routes due to the presence of reducing agents and other stabilizing and capping agents (Jadoun et al., 2021). As NPs fabrication includes the use of plant extracts, animal proteins, agro-waste, pigments, bacterial cultures, fungal samples, and small viruses, which are difficult to handle with conventional methods, green synthesis of nanoparticles is widely recommended. All these biological objects also include bioactive metabolites such as proteins, polysaccharides, aldehydes, ketones, carboxylic acids, polyphenols, tannins, flavonoids, saponins, terpenoids, amines, and alkaloids, which serve as bio- reducing, stabilizing, and capping agents and are capable of transforming metallic ions into plasmonic NPs, synthesizing required NPs with previously reported beneficial properties (Naveed et al., 2022).

Although the rapid and eco-friendly green synthetic routes using biological extracts have shown their great potential in NPs fabrication, the mechanism by which bioactive metabolites are involved in the synthesis and the mode of plasmonic properties is still not fully understood. In addition, controlling the size range and morphology of green synthesized NPs, which has many positive effects on its capabilities, remained largely unanswered till today, although chemical methods are already well-known for shape-controlled synthesis (Vanlalveni et al., 2021).

Green (bio-) synthesis, which harnesses the power of biological extracts, has surfaced as a promising alternative. However, green methods face challenges, including prolonged processing times and a reduced ability to control nanoparticle size, morphology, and crystallinity (Secario et al., 2024). Despite these limitations, green-synthesized NPs are increasingly recognized for their potential to mitigate environmental challenges while offering promising avenues in the field of medicine, in the agro-industrial complex, and ecological science. The long-term stability can also be impacted by strict control of temperature, light, and pH levels, which can alter how well they could work in different applications. The wider use and commercialization of green-synthesized AgNPs depend on addressing these issues through more research and development (Dheyab et al., 2025).

In general, the world faces threats that the United Nations has ranked as global problems of humanity into 17 categories with various objectives as solutions for each challenge that are enclosed in the Sustainable Development Goals (SDGs). These responsive solutions involved the prevalence of science and technology as pathways to ensure their implementation. In this regard, sustainability science seeks the research community's contribution to addressing sustainable development challenges. Specifically, green and eco-friendly nanotechnology has been recognized as a key tool for potential applications in disruptive and effective strategies to reach the SDGs (Larrañaga-Tapia et al., 2024).

Nevertheless, statistical data analysis (see Fig. 4) depicted the increasing trend of published research articles in the field of green synthesis of metallic NPs. These data were collected from the National Center for Biotechnology Information (NCBI) using the keywords "Green synthesis of nanoparticles" in the PubMed database. From a meager number of 689 publications in the year of 2015, it has exponentially increased to 2032 publications in 2024.

Conclusions

The steady growth of interest in the field of green synthesized NPs can be used for development of a

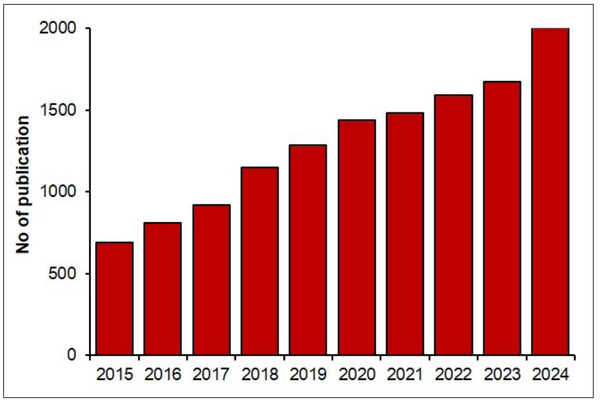

Fig. 4. Publications number per year for green synthesis of NPs since 2015 to 2024 (data collected from the NCBI PubMed database)

TNT and other explosives determination procedure that is simple, rapid, and sensitive, which can be applied for the identification of explosive threats and contaminations for the implementation of the Ukraine's Recovery Plan (https://www.urc-international.com/past-conferences/urc22/urc2022-recovery-plan). In contrast to conventional Raman spectroscopy, SERS enables the detection of molecules even in minute concentrations in solutions or when deposited onto nanostructured noble metal films. This technique can be used to detect contamination in air, soils, and water sources.

At the same time, as the war continues, there are constant massive missile and drone attacks throughout Ukraine, and significant areas remain occupied in the southeast of Ukraine, creating enormous difficulties for research, education, and business. The scientific community in Ukraine has an urgent need to address long-term challenges, to retain its high standards of research and technology and to develop new ideas under the current circumstances (Duszyński et al., 2022; Kondratov et al., 2022).

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ETHICS DECLARATION

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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REFERENCES

Abdelmigid H.M., Hussien N.A., Alyamani A.A., Morsi M.M., AlSufyani N.M., Kadi H.A. 2022. Green synthesis of zinc oxide nanoparticles using pomegranate fruit peel and solid coffee grounds vs. chemical method of synthesis, with their biocompatibility and antibacterial properties investigation. *Molecules*, 27(4): 1236. https://doi.org/10.3390/molecules27041236

Alharbi N.S., Alsubhi N.S., Felimban A.I. 2022. Green synthesis of silver nanoparticles using medicinal plants: Characterization and application. *Journal of Radiation Research and Applied Sciences*, 15(3): 109–124. https://doi.org/10.1016/j.jrras.2022.06.012

Alizadeh N., Yoosefian J. 2023. Chemical reduction as a facile colorimetric approach for selective TNT detection by spectrophotometry and photothermal lens spectroscopy. *Talanta*, 257: 124334. https://doi.org/10.1016/j.talanta.2023.124334

Apak R., Üzer A., Sağlam Ş., Arman A. 2023. Selective electrochemical detection of explosives with nanomaterial based electrodes. *Electroanalysis*, 35(1): e202200175. https://doi.org/10.1002/elan.202200175

Álvarez-Chimal R., Arenas-Alatorre J.Á. 2023. Green synthesis of nanoparticles. A biological approach. In: *Green Chemistry for Environmental Sustainability — Prevention-Assurance-Sustainability (P-A-S) Approach*. Ed. K.J. Shah. IntechOpen. https://doi.org/10.5772/intechopen.1002203

Awasthi G., Sharma R., Sundarrajan S., Ramakrishna S., Kumar P. 2022. Progressive trends in hybrid material-based chemiresistive sensors for nitroaromatic compounds. *Polymers*, 14(21): 4643. https://doi.org/10.3390/polym14214643

Banas A.M., Banas K., Breese M.B. 2023. Classification of the residues after high and low order explosions using machine learning techniques on Fourier Transform Infrared (FTIR) spectra. *Molecules*, 28(5): 2233. https://doi.org/10.3390/molecules28052233

Bener M., Şen F.B., Apak R. 2022. Protamine gold nanoclusters–based fluorescence turn-on sensor for rapid determination of Trinitrotoluene (TNT). *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 279: 121462. https://doi.org/10.1016/j.saa.2022.121462

Borovaya M., Horiunova I., Plokhovska S., Pushkarova N., Blume Y., Yemets A. 2021. Synthesis, properties and bioimaging applications of silver-based quantum dots. *International Journal of Molecular Sciences*, 22: 12202. https://doi.org/10.3390/ijms222212202

Chegel V.I., Lopatynskyi A.M., Lytvyn V.K., Demydov P.V., Martínez-Pastor J.P., Abargues R., Gadea E.A., Piletsky S.A. 2020. Localized surface plasmon resonance nanochips with molecularly imprinted polymer coating for explosives sensing. *Semiconductor Physics, Quantum Electronics and Optoelectronics*, 2(4): 431–436. https://doi.org/10.15407/spqeo23.04.431

Chio W.I.K., Peveler W.J., Assaf K.I., Moorthy S., Nau W.M., Parkin I.P., Lee T.C. 2019. Selective detection of nitroexplosives using molecular recognition within self-assembled plasmonic nanojunctions. *The Journal of Physical Chemistry C*, 123(25): 15769–15776. https://doi.org/10.1021/acs.jpcc.9b02363

Demydov P.V., Lopatynskyi A.M., Hudzenko I.I., Chegel V.I. 2021. The approaches for localized surface plasmon resonance wavelength position tuning. Short review. *Semiconductor Physics, Quantum Electronics and Optoelectronics*, 24: 304–311. https://doi.org/10.15407/spqeo24.03.304

Devi S., Garg V., Tyagi S. 2022. Amino benzene dicarboxylic acid-derived luminescent nitrogen-doped carbon-quantum dots/anti-TNT antibodies conjugate for detection of nitroaromatic contaminant in water: A comparative analysis of chemo-bio-sensing affinity. *Microchemical Journal*, 181: 107607. https://doi.org/10.1016/j.microc.2022.107607

Dheyab M., Aziz A., Nowfal S., Braim F., Abdullah W., Kasasbeh W., Oladzadabbasabadi N. 2025. Sustainable green synthesis of silver nanoparticles for safer biomedical application. *Journal of Environmental Chemical Engineering*, 13(2): 115998. https://doi.org/10.1016/j.jece.2025.115998

Duszyński J., McNutt M., Zagorodny A. 2022. A future for Ukrainian science. *Science*, 376(6599): 1249–1249. https://doi.org/10.1126/science.add4088

Dzhagan V.M., Pirko Y.V., Buziashvili A.Y., Plokhovska S.G., Borova M.M., Yemets A.I., Yukhymchuk V.O. 2022a. Controlled aggregation of plasmonic nanoparticles to enhance the efficiency of SERS substrates. *Ukrainian Journal of Physics*, 67: 80–87. https://doi.org/10.15407/ujpe67.1.80

Dzhagan V., Smirnov O., Kovalenko M., Mazu, N., Hreshchuk O., Taran N., Zahn D.R.T. 2022b. Spectroscopic study of phytosynthesized Ag nanoparticles and their activity as SERS substrate. *Chemosensors*, 10(4): 129. https://doi.org/10.3390/chemosensors10040129

Dzhagan V., Mazur N., Smirnov O., Yeshchenko O., Isaieva O., Kovalenko M., Valakh M. 2023. SERS application of Ag nanoparticles synthesized with aqueous fungi extract. *Journal of Nanoparticle Research*, 25(3): 37. https://doi.org/10.1007/s11051-023-05683-9

Elsayed M.S., Ahmed I.A., Bader D., Hassan A.F. 2022. Green synthesis of nano zinc oxide/nanohydroxyapatite composites using date palm pits extract and eggshells: adsorption and photocatalytic degradation of methylene blue. *Nanomaterials*, 12(1): 49. https://doi.org/10.3390/nano12010049

Fagier M.A. 2021. Plant-mediated biosynthesis and photocatalysis activities of zinc oxide nanoparticles: a prospect towards dyes mineralization. *Journal of Nanotechnology*, 21: 1–15. https://doi.org/10.1155/2021/6629180

Gao R., Qian H., Weng C., Wang X., Xie C., Guo K., Luo L.B. 2020. A SERS stamp: Multiscale coupling effect of silver nanoparticles and highly ordered nano-micro hierarchical substrates for ultrasensitive explosive detection. *Sensors and Actuators B: Chemical*, 321: 128543. https://doi.org/10.1016/j.snb.2020.128543

Gao W., Wang T., Zhu C., Sha P., Dong P., Wu X. 2022. A 'sandwich' structure for highly sensitive detection of TNT based on surface-enhanced Raman scattering. *Talanta*, 236: 122824. https://doi.org/10.1016/j.talanta.2021.122824

Gong Z., Du H., Cheng F., Wang C., Wang C.-C., Fang M. 2014. Fabrication of SERS swab for direct detection of trace explosives in fingerprints. *ACS Applied Materials & Interfaces*, 6: 21931–21937. https://doi.org/10.1021/am507424v

Graham D., Goodacre R., Arnolds H. 2017. Theory of SERS enhancement: general discussion. *Faraday Discuss*, 205: 173–211. https://doi.org/10.1039/C7FD90095C

Habeeb Rahuman H.B., Dhandapani R., Narayanan S., Palanivel V., Paramasivam R., Subbarayalu R., Muthupandian S. 2022. Medicinal plants mediated the green synthesis of silver nanoparticles and their biomedical applications. *IET Nanobiotechnology*, 16(4): 115–144. https://doi.org/10.1049/nbt2.12078

Hiraoka K., Takaishi R., Ninomiya S., Rankin-Turner S. 2023. Electrospray droplet impact/secondary ion mass spectrometry (EDI/SIMS) applied to the analysis of explosives. *International Journal of Mass Spectrometry*, 484: 116993. https://doi.org/10.1016/j.ijms.2022.116993

Hu Z., Peng D., Xing F., Wen X., Xie K., Xu X., Fan M. 2023 Iodine-modified Ag NPs for highly sensitive SERS detection of deltamethrin residues on surfaces. *Molecules*, 28(4): 1700. https://doi.org/10.3390/molecules28041700

Jadoun S., Arif R., Jangid N.K., Meena R.K. 2021. Green synthesis of nanoparticles using plant extracts: A review. *Environmental Chemistry Letters*, 19: 355–374. https://doi.org/10.1007/s10311-020-01074-x

Jamil A.K., Izake E.L., Sivanesan A., Fredericks P.M. 2015. Rapid detection of TNT in aqueous media by selective label free surface enhanced Raman spectroscopy. *Talanta*, 134: 732–738. https://doi.org/10.1016/j.talanta.2014.12.022

Johnston E.J., Rylott E.L., Beynon E., Lorenz A., Chechik V., Bruce N.C. 2015. Monodehydroascorbate reductase mediates TNT toxicity in plants. *Science*, 349(6252): 1072–1075. https://doi.org/10.1126/science.aab3472

Junaid H.M., Waseem M.T., Khan Z.A., Gul H., Yu C. Shaikh A.J., Shahzad S.A. 2022. Fluorescent and colorimetric sensors for selective detection of TNT and TNP explosives in aqueous medium through fluorescence emission enhancement mechanism. *Journal of Photochemistry and Photobiology A: Chemistry*, 428: 113865. https://doi.org/10.1016/j.jphotochem.2022.113865

Karadurmus L., Bilge S., Sınağ A., Ozkan S.A. 2022. Molecularly imprinted polymer (MIP)-based sensing for detection of explosives: Current perspectives and future applications. *TrAC Trends in Analytical Chemistry*, 116694. https://doi.org/10.1016/j.trac.2022.116694

Klapec D., Czarnopys, G., Pannuto J. 2023. Interpol review of the analysis and detection of explosives and explosives residues. *Forensic Science International: Synergy*, 6: 100298. https://doi.org/10.1016/j.fsisyn.2022.100298

Kneipp K., Wang Y., Dasari R.R., Feld M.S., Gilbert B.D., Janni J., Steinfeld J.I. 1995. Near-infrared surface-enhanced Raman scattering of trinitrotoluene on colloidal gold and silver. *Spectrochimica Acta Part A*, 51: 2171–2175. https://doi.org/10.1016/0584-8539(95)01474-7

Kondratov I.S., Moroz Y.S., Gorgulla C., Grygorenko O.O., Komarov I.V., Wagner G., Tolmachev A.A. 2022. Challenges for chemistry in Ukraine after the war: Ukrainian science requires rebuilding and support. *Proceedings of the National Academy of Sciences*, 119(50): e2210686119. https://doi.org/10.1073/pnas.2210686119

Langer J., Jimenez de Aberasturi D., Aizpurua J., Alvarez-Puebla R.A., Auguié B., Baumberg J.J., Bazan G.C., Bell S.E., Boisen A., Brolo A.G., Choo J. et al. 2019. Present and future of surface-enhanced Raman scattering. *ACS Nano*, 14(1): 28–117. https://doi.org/10.1021/acsnano.9b04224

Larrañaga-Tapia M., Betancourt-Tovar B., Videa M., Antunes-Ricardo M., Cholula-Díaz J.L. 2024. Green synthesis trends and potential applications of bimetallic nanoparticles towards the sustainable development goals 2030. *Nanoscale Advances*, 6(1): 51–71. https://doi.org/10.1039/D3NA00761H

Li L., Gu H., Lv Y., Zhang Y., He X., Li P. 2022. Ultra-fast polarity switching, non-radioactive drift tube for the miniaturization of drift-time ion mobility spectrometer. *Sensors*, 22(13): 4866. https://doi.org/10.3390/s22134866

Li X., Zhao X., Xu X., Lu Y., Wu J., Liu F., Lu G. 2023. Excitation orthogonalized upconversion nanoprobe for instant visual detection of trinitrotoluene. *Nano Research*, 16(1): 1491–1499. https://doi.org/10.1007/s12274-022-4693-8

Liu W., Song Z., Zhao Y., Liu Y., He X., Cui S. 2020. Flexible porous aerogels decorated with Ag nanoparticles as an effective SERS substrate for label-free trace explosives detection. *Analytical Methods*, 12(33): 4123–4129. https://doi.org/10.1039/D0AY00771D

Llorente V.B., Dzhagan V.M., Gaponik N., Iglesias R.A., Zahn D.R.T., Lesnyak V. 2017. Electrochemical tuning of localized surface plasmon resonance in copper chalcogenide nanocrystals. *Journal of Physical Chemistry C*, 121: 18244–18253. https://doi.org/10.1021/acs.jpcc.7b05334

Mazur N., Dzhagan V., Kapush O., Isaieva O., Demydov P., Lytvyn V., Yukhymchuk V. 2025. SERS of nitro group compounds for sensing of explosives. *RSC Advances*, 15(1): 252–260. https://doi.org/10.1039/D4RA07309F

Mata Y.N., Torres E., Blazquez M.L., Ballester A., González F.M.J.A., Munoz J.A. 2009. Gold (III) biosorption and bioreduction with the brown alga *Fucus vesiculosus*. *Journal of Hazardous Materials*, 166(2–3): 612–618. https://doi.org/10.1016/j.jhazmat.2008.11.064

Malik K., Kazmi A., Sultana T., Raja N.I., Bibi Y., Abbas M., Badruddin I.A., Ali M.M., Bashir M.N. 2025. A mechanistic overview on green assisted formulation of nanocomposites and their multifunctional role in biomedical applications. *Heliyon*, 11(3): e41654. https://doi.org/10.1016/j.heliyon.2025.e41654

Meera C.R., Zaynitdinova L., Great U. 2025. Sustainable production of nanoparticles from fungi and their agricultural applications. In: Mohanta Y.K., Mishra B., Pudake R.N. (eds). *Nano-microbiology for Sustainable Development*. Cham: Springer. https://doi.org/10.1007/978-3-031-78845-1_4

Naveed M., Bukhari B., Aziz T., Zaib S., Mansoor M.A., Khan A.A., Alhomrani M. 2022. Green synthesis of silver nanoparticles using the plant extract of *Acer oblongifolium* and study of its antibacterial and antiproliferative activity via mathematical approaches. *Molecules*, 27(13): 4226. https://doi.org/10.3390/molecules27134226

Pandit C., Roy A., Ghotekar S., Khusro A., Islam M.N., Emran T.B., Bradley D.A. 2022. Biological agents for synthesis of nanoparticles and their applications. *Journal of King Saud University-Science*, 34(3): art. 101869. https://doi.org/10.1016/j.jksus.2022.101869

Rozo J.I.J., Chamoun A.M., Peña S.L., Hernández-Rivera S.P. 2007. Enhanced Raman scattering of TNT on nanoparticle substrates: Ag colloids prepared by reduction with hydroxylamine hydrochloride and sodium citrate. In: *Sensors, and Command, Control, Communications, and Intelligence (C3I) Technologies for Homeland Security and Homeland Defense VI (9–12 Orlando, Florida, USA).Proceedinds of SPIE*. Vol. 6538. Ed. E.M. Carapezza. Bellingham: SPIE, 653824: 487–498. https://doi.org/10.1117/12.746436

Samuel M.S., Ravikumar M., John J.A., Selvarajan E., Patel H., Chander P.S., Chandrasekar N. 2022. A review on green synthesis of nanoparticles and their diverse biomedical and environmental applications. *Catalysts*, 12(5): 459. https://doi.org/10.3390/catal12050459

Secario M., Truong T., Chen C., Lai J., Lue S. 2024. Size-dependent antibacterial efficacy of silver nanoparticles from a green synthesis method: Effects of extract quantity and origin. *Journal of the Taiwan Institute of Chemical Engineers*, 161: 105511. https://doi.org/10.1016/j.jtice.2024.105511

Silarski M., Nowakowski M. 2022. Performance of the SABAT neutron-based explosives detector integrated with an unmanned ground vehicle: a simulation study. *Sensors*, 22(24): 9996. https://doi.org/10.3390/s22249996

Smirnov O., Kalynovskyi V., Yumyna Y., Zelena P., Levenets T., Kovalenko M., Dzhagan V., Skoryk M. 2022. Potency of phytosynthesized silver nanoparticles from *Lathraea squamaria* as anticandidal agent and wheat seeds germination enhancer. *Biologia*, 77(9): 2715–2724. https://doi.org/10.1007/s11756-022-01117-4

Smirnov O., Dzhagan V., Kovalenko M., Gudymenko O., Dzhagan V., Mazur N., Isaieva O., Maksimenko Z., Kondratenko S., Skoryk M., Yukhymchuk V. 2023a. ZnO and Ag NPs-decorated ZnO nanoflowers: green synthesis using *Ganoderma lucidum* aqueous extract and characterization. *RSC Advances*, 13: 756–763. https://doi.org/10.1039/D2RA05834K

Smirnov O., Dzhagan V., Yeshchenko O., Kovalenko M., Vuichyk M., Dzhagan V., Mazur N., Skoryk M., Yukhymchuk V. 2023b. Effect of pH of *Ganoderma lucidum* aqueous extract on green synthesis of silver nanoparticles. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 14(3): 035009. https://doi.org/10.1088/2043-6262/acebd4

Son C.E., Choi S.S. 2023. Deprotonation of trinitrotoluene by dichloromethane in atmospheric pressure chemical ionization mass spectrometry. *Rapid Communications in Mass Spectrometry*, 37(3): e9434. https://doi.org/10.1002/rcm.9434

Stefancu A., Iancu S.D., Moisoiu V., Leopold N. 2018. Specific and selective SERS active sites generation on silver nanoparticles by cationic and anionic adatoms. *Romanian Reports in Physics*, 70: 509.

To K.C., Ben-Jaber S., Parkin I.P. 2020. Recent developments in the field of explosive trace detection. *ACS Nano*, 14(9): 10804–10833. https://doi.org/10.1021/acsnano.0c01579

Vanlalveni C., Lallianrawna S., Biswas A., Selvaraj M., Changmai B., Rokhum S.L. 2021. Green synthesis of silver nanoparticles using plant extracts and their antimicrobial activities: A review of recent literature. *RSC Advances*, 11(5): 2804–2837. https://doi.org/10.1039/D0RA09941D

Xu M., He L., Sun P., Wu M., Cui X., Liu D., Maser E. 2023. Critical role of monooxygenase in biodegradation of 2,4,6-trinitrotoluene by *Buttiauxella* sp. S19-1. *Molecules*, 28(4): 1969. https://doi.org/0.3390/molecules28041969

Xu M-L., Gao Yu., Han X-X., Zhao B. 2017. Detection of pesticide residues in food using surface-enhanced Raman spectroscopy: A review. *Journal of Agricultural and Food Chemistry*, 65: 6719–6726. https://doi.org/10.1021/acs.jafc.7b02504

Xu M-L., Gao Yu., Han X-X., Zhao B. 2022. Innovative application of SERS in food quality and safety: A brief review of recent trends. *Foods*, 11: 2097. https://doi.org/10.3390/foods11142097

Yang X., Zhang Y., Lai J.L., Luo X.G., Han M.W., Zhao S.P., Zhu Y.B. 2021. Analysis of the biodegradation and phytotoxicity mechanism of TNT, RDX, HMX in alfalfa (*Medicago sativa*). *Chemosphere*, 281: 130842. https://doi.org/10.1016/j.chemosphere.2021.130842

Ying S., Guan Z., Ofoegbu P.C., Clubb P., Rico C.H.F., Hong J. 2022. Green synthesis of nanoparticles: Current developments and limitations. *Environmental Technology & Innovation*, 26: 102336. https://doi.org/10.1016/j.eti.2022.102336

Zapata F., López-López M., García-Ruiz C. 2016. Detection and identification of explosives by surface enhanced Raman scattering. *Applied Spectroscopy Reviews*, 51(3): 227–226. https://doi.org/10.1080/05704928.2015.1118637

Високий потенціал біосинтезованих наночастинок як ефективного та дешевого засобу для SERS-виявлення вибухових речовин на основі тринітротолуолу

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Реферат. Цей огляд присвячений обговоренню питання подолання наслідків російського вторгнення в Україну та дослідженням щодо вирішення проблеми забруднення вибуховими речовинами, такими як 2,4,6-тринітротолуол (TNT). Для забезпечення захисту цивільного та військового населення надзвичайно важливою є розробка простої, швидкої та чутливої процедури визначення цих речовин, яку можуть використовувати служби першого реагування на місці для виявлення загрози TNT для навколишнього середовища або безпеки людей. Поверхнево-підсилене комбінаційне розсіяння світла (SERS) вважається новим методом детекції з високою чутливістю, високою специфічністю та швидкою реакцією, який успішно застосовувався для біохімічного виявлення токсичних аналітів або забруднювачів навколишнього середовища. При цьому показано, що синтезовані зеленим шляхом металеві наночастинки рослинного та грибного походження здатні посилювати сигнал SERS від різних речовин, з можливістю реєстрації спектру SERS від однієї цільової молекули. Загальний метод синтезу наночастинок на основі рослин та грибів є таким: спочатку обирають рослинний чи грибний матеріал, подрібнюють і отримують екстракт, який обробляють для видалення будь-яких домішок; потім попередник, зазвичай розчин металовмісної солі, змішують із рослинним екстрактом, що призводить до отримання наночастинок. Підтримка відповідного рівня рН, температури та безперервне перемішування, що забезпечує отримання наночастинок рівномірного розміру, має вирішальне значення для ефективного протікання синтезу. Поєднання доступного і сталого виробництва та високих аналітичних можливостей робить таку наноструктуру перспективною для досліджень і дезактивації значних територій України, уражених вибухонебезпечними сполуками та продуктами їхнього розпаду.

Ключові слова: детекція тринітротолуолу, зелений синтез, локалізований плазмонний резонанс, металічні наночастинки, SERS підкладки