SYNTHESIS AND CHARACTERIZATION OF NITRIC OXIDE DONOR NANOSTRUCTURED DENDRITIC MESOPOROUS TETRASULFIDE-BRIDGED ORGANOSILICA WITH PROSPECTS FOR ENVIRONMENTAL APPLICATION

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Abstract

The objective of this study was to develop and optimize nanomaterials capable of enhancing the essential parameters of plant growth. To achieve this objective, nanoparticle-based nitric oxide (NO) donors and graphene oxide quantum dots (GQDs) were synthesized. Carbon quantum dots and graphene quantum dots (GQDs) exhibit minimal inhibition of the natural growth pathways of plants and have demonstrated potential to enhance growth while maintaining good biocompatibility. The NO donor was designed as nanostructured dendritic mesoporous tetrasulfide-bridged organosilica nanoparticles (DMON NPs), which have been modified with S-nitrosothiol (SNO) to facilitate a controlled and sustained release of NO. These characterizations are crucial to assess comprehensively the performance and potential applications of the nanoparticles in agricultural and plant biotechnology contexts.

Introduction

In response to various biotic (e.g., herbivores, pathogens, insects) and abiotic stress factors (e.g., drought, heavy metals, salinity), plants produce several redox molecules through enzymatic reactions to defend themselves. These highly reactive molecules, encompassing both free radicals and non-radical derivatives, include reactive oxygen species (ROS) and reactive nitrogen species (RNS). Although the excessive accumulation of these molecules can lead to oxidative burst, they are essential for homeostasis, self-defense, development, and hormonal signaling. Among the reactive oxygen and nitrogen species, nitric oxide (NO) is a predominant RNS. It is a diatomic, gaseous, uncharged free radical with a short lifespan, capable of migrating through both hydrophilic and hydrophobic regions of the cells (its existence spans three redox-active forms). NO rapidly reacts with other radicals and several other molecules. A notable example is its interaction with glutathione (GSH), to form a highly stable compound known as S-nitrosoglutathione (GSNO), which serves as a significant reservoir of NO within cells.
However, the controlled delivery of NO to plants remains a challenge due to its instability and transient nature. For effective NO delivery in agricultural systems, dendritic mesoporous tetrasulfide-bridged organosilica nanoparticles (DMON) with S-nitrosothiol modification (DMON-SNO) were designed (Fig. 1).

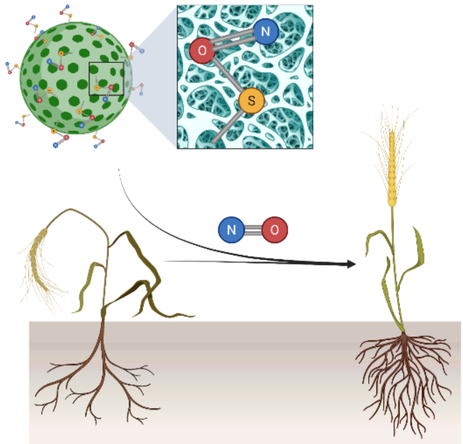

Fig 1.: Shematic figure of DMON-SNO and its effect to plant development as nitric oxide

Experimental

The DMON NPs were synthesized following a reported protocol. Firstly 380 mg of CTAB and 168 mg NaSal were added to the mixture of 25 ml deionized water and 68 mg of TEA. After this, 2 ml of TEOS and 1 ml of BTES were added and the mixture was vigorously stirred overnight at 80 °C. After an extraction of surfactant with 40 ml methanol and NaCl (25wt%) the product was centrifugated and collected.

For thiol modification 15 mg of the product was dispersed in 5 ml of ethanol. 150 µl ammonium hydroxid (30 wt%) and 200 µl MPTMS were added and stirred overnight at room temperature. The products were collected and washed with ethanol. For S-nitrosothiol modification 5 mg of these NPs were dispersed in 400 µl of methanol and 200 µl of 5 M HCl and stirred on ice. After cooling, a solution of 16 mg of $NaNO_2$ and 200 µl of DTPA (500 µM aqueous solution) was added to the mixture and stirred for 1 hour in dark and on ice. The DMON-SNO products were collected and washed twice with DTPA and methanol.

Results and discussion

The successful syntheses of DMON nanoparticles were validated using several physicochemical characterization methods including transmission electron microscopy (TEM), X-ray diffraction (XRD), dynamic light scattering (DLS) and ultraviolet-visible spectroscopy (UV-Vis) measurements (Fig. 2).

The chraracteristic of XRD pattern show one wide peak with spacings *d* of 21,36 Å. This large distance is characteristic of the mesostructure (pore structure).

Transmission electron microscopy was utilized to determine the size and morphological characteristics of the nanoparticles, with results detailed in Fig. 2B. The DMON nanoparticles were found to be spherical in shape, with an average size of approximately 200 nm.

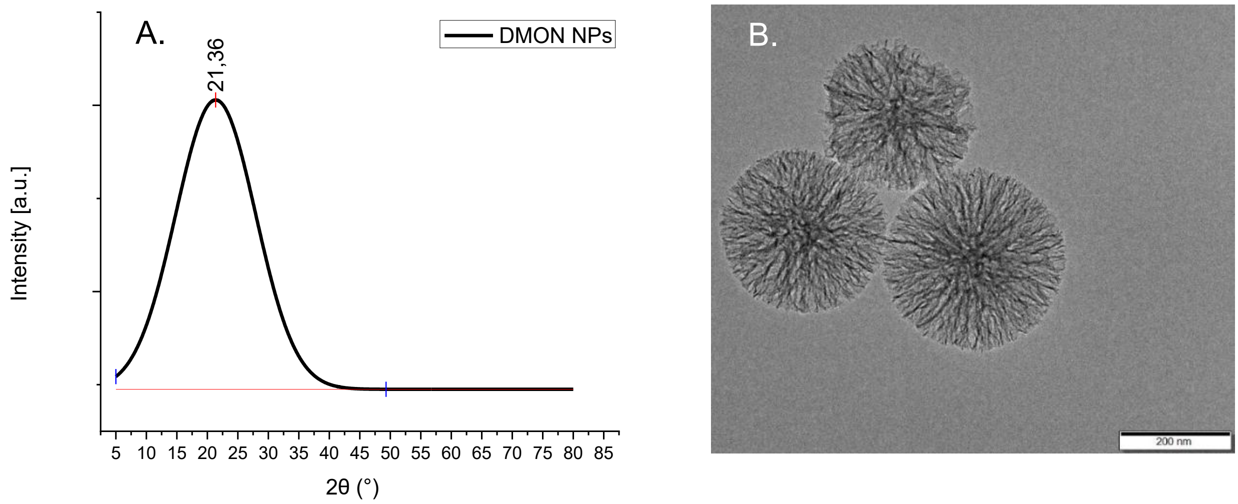

Fig 2.: A. X-ray diffraction pattern of DMON NPs;
B. Transmission electron microscopy image of DMON NPs

Ultraviolet-visible spectroscopy facilitated the measurement of localized surface plasmon resonance, revealing peaks at 320.75, 447.8, and 875.40 nm, which are consistent with values reported in the literature. Following thiol modification, new peaks emerged within the 478-528 nm range, confirming the successful functionalization, as illustrated in Fig. 3. The nitroso thiol modification was successful according to the color change of the product however the release speed needed to be examined further. Moreover the color was disappeared after a day. Dynamic light scattering analysis indicated that nanoparticles predominantly had a diameter of 220 nm and they exhibited a zeta potential of -11.4 mV.

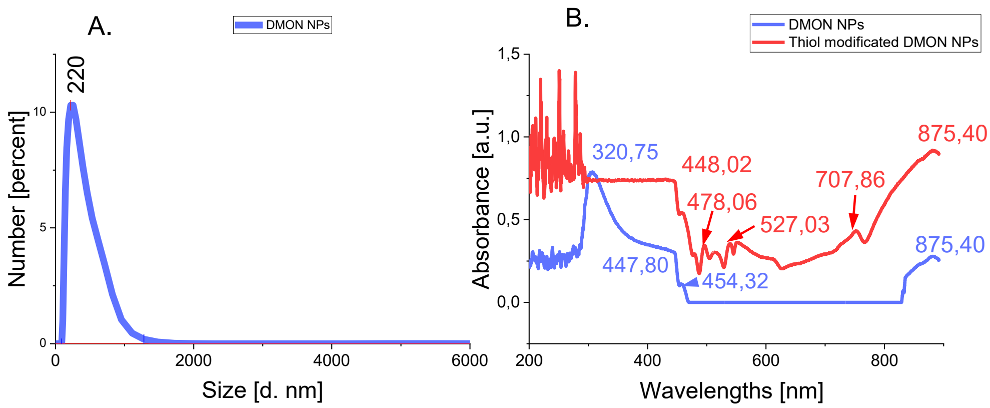

Fig 3.: A. Dimanic light scattering size distribution of DMON NPs by number; B. UV- visible light absorption spectra of DMON NPs and thiol miodified DMON NPs

Conclusion

In conclusion, this study demonstrated the succesful synthesis of dendritic mesoporous tetrasulfide-bridged organosilica. The products were homogeneous and spherical shaped, which were verified by dynamic light scattering and transmission electron microscopy measurements.

The product was suitable for both thiol and S- nitrosothiol modification. However, the release rate and ratio of NO content require further investigation. The UV-VIS characterisation results revealed distinct spectral peaks corresponding to both the modified forms and the initial DMON. This research anticipates the promising applications of DMON-SNO in promoting plant growth and development via the functional benefits of NO.

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