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Impact of smart combinations of graphene oxide and micro/nanosized sulfur particles on soil health and plant biomass accumulation

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Abstract

Background: Elemental sulfur (S^0) is a cost-efficient fertilizer and the least rapidly utilizable source of S for soil microorganisms and plants. Its bacterial-mediated oxidation to sulfates is dependent on particle size. Finely formulated (micronized, nanosized) S^0 exerts enhanced oxidation rate and benefit due to nutrient availability and crop nutrition efficiency. Graphene oxide (GO) affects soil properties both negatively and positively. A pot experiment was carried out with lettuce using soil supplemented with S^0 in different composition, applied alone or in combination with GO. The following variants were tested: control, GO, micro- S^0 , micro- S^0 + GO, nano- S^0 , nano- S^0 + GO.

Results: Nanosized S^0 improved most of enzyme activities (dehydrogenase, arylsulfatase, *N*-acetyl- β -D-glucosaminidase, β -glucosidase, phosphatase). However, respirations induced by D-glucose, protocatechuic acid, L-arginine were decreased. GO mitigated negative to neutral effect of micro- S^0 in the soil pH, dehydrogenase and urease activity. Furthermore, micro- S^0 positively affected basal respiration and respirations induced by D-trehalose and *N*-acetyl- β -D-glucosamine. Nano- S^0 + GO improved plant biomass yield and enzyme activities. However, nano- S^0 + GO significantly decreased all substrate-induced respirations.

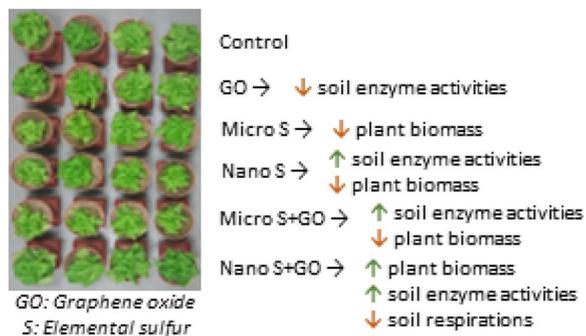
Conclusions: The benefit of soil treatment with nano-/micro-sized S^0 and its combination with GO on soil biological parameters was partially demonstrated.

Keywords: Elemental sulfur, Graphene oxide, Soil enzyme activities, Soil respiration

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Graphical Abstract



Background

Sulfur, an essential albeit secondary element forms amino acids, proteins, plant oils, is involved in chlorophyll synthesis, promotes nodulation in legumes, helps develop and activate certain enzymes and vitamins [1]. There are several types of sulfur-based fertilizers available and applied in either conventional or sustainable agro-management systems. These fertilizers contain various forms of sulfur, in particular: sulfates (ammonium, potassium, magnesium and calcium sulfate), thiosulfate (ammonium and potassium thiosulfate), elemental sulfur [2] and fertilizer based on polysulfides. Most sulfur fertilizers are applied to the soil, many can also be used for foliar application [3]. Elemental sulfur (S^0) possesses several properties which make this material beneficial in agriculture application. S^0 promotes tolerance to several biotic and abiotic stresses in plants [4]. In contrast to sulfates, S^0 is insoluble [2], which partially prevents its leaching [5, 6] after its application to the soil. However, after oxidation by bacteria to sulfates (SO_4^{2-}), it is usable as a source of nutrients for organisms and plants [7]. The oxidation process is dependent on the function of specific taxa in soil microbiome, represented mainly by genus *Thiobacillus* [8] and *Betaproteobacteria* [9]. On the contrary, elemental sulfur has a biocidal effect on some soil microorganisms, mainly fungi [10, 11]. The process of S^0 oxidation in soil and conversion to a available form further depends on soil temperature, water potential, soil aeration [8], as well as on hydrophobicity of S^0 particles, which significantly depends on their size [12]. Smaller S^0 particles undergo accelerated oxidation, the increase in particle size decelerates the conversion [13].

In agriculture, fine formulated (micronized, nano-sized) S^0 is used to increase its oxidation rate [14] and enhance its effectiveness in heavy metal toxicity alleviation [15], alteration of soil pH [16], nutrient availability [17], plant nutrition efficiency [18, 19], and plant pests

control [20]. The micro-/nanosized S^0 is obtained from the coarser formulated particles by crushing, ball milling [21, 22] or sonication [23]. Furthermore, the properties of the powdered S^0 could be improved by combination with other types of materials. Graphene- or 2D carbon-based nanomaterials, such as graphene oxide (GO) and reduced graphene oxide, are carbonaceous nanomaterials, which have been widely used for environmental (soil, water) applications to mitigate various pollutants [24, 25]. Although GO was reported to negatively affect the growth and abundance of specific soil microbial community groups [26–30], some studies showed also neutral to positive effect of GO on microbiome [31, 32] and biological soil properties [33], as well as on plant growth and physiology [34, 35]. Combining GO with other elemental nanoparticles is considered promising, because this approach improves properties of GO [36] and grants new qualities to the obtained material [37, 38]. The benefit of combining GO or other carbon-rich materials with S^0 was also noted in technology sectors, e.g., electrical engineering [39], but also in environmental and forestry applications [40, 41]. Since a positive supporting effect of carbon matrix (graphite plate) on the biofilm development of *Acidithiobacillus thiooxidans* due to the increased adherence of S^0 particles to the graphite surface was observed, we expected a reciprocal stimulatory effect of $GO + S^0$ on the abundance and activity of specific S^0 -oxidating microbiome in amended soil and increased rate of transformation to the plant-available form of S (sulfates). However, the studies regarding the effects of nanosized S^0 on soil health indicators have been limited in previous literature. The sparse reports available hitherto have only focused on its individual application in the soil. However, the effects of the combined application of differently sized S^0 and GO on soil respiration (basal as well substrate induced) and soil extracellular enzymes

activity have remained largely overlooked which in the present study constitute the novelty of this work.

Therefore, taking the above background into account we hypothesized that:

- I. S^0 would improve soil biological properties, i.e., microbial biomass and activity in a particle size-dependent way.
- II. GO would interact with elemental sulfur and change S^0 -traits to mitigate its intrinsic negative impact (acidification, possible fungistatic effect) and further increase S^0 -mediated transformation rate of soil organic matter (SOM), followed by higher lettuce biomass yield.

The specific objectives of this study were thus to evaluate the effect of soil application of S^0 (micro, nano), GO, and their composite on the plant growth and biomass accumulation, and soil chemical and biological health indicators.

Materials and methods

Sources and preparation of materials

Demineralized water was produced using an Aqual 25 reverse osmosis apparatus (Aqual, Česká, Czech Republic) and further treated with Millipore System Inc. (BillERICA, MA, USA) to obtain ultrapure water with the corresponding resistivity of 18.2 M Ω cm (at 25 °C). All experiments used ultrapure water unless otherwise stated. The pH values were evaluated using a pH meter (WTW inoLab, Weilheim, Germany) with WTW SenTix pH electrode. The synthesis of GO was previously detailed described in [42]. Sulfur nanoparticles in water dispersion were purchased from US Research Nanomaterials, Inc (Houston, TX, USA). Sulfur micropowder was purchased from Genetrix (Bohumín, Czech Republic).

The nanocomposites of GO with sulfur were synthesized by the following procedures. For nano- S^0 +GO, 25 mL of GO (2 g·L⁻¹) was mixed with 50 mL of nano- S^0 (100 g·L⁻¹) and a filled up to 500 mL with ultrapure water. For GO+micro- S^0 , 5 g of micro- S^0 were placed into 500 mL flask with 25 mL of GO (2 g·L⁻¹) and filled up to 500 mL with ultrapure water. The final concentration of both suspensions was: 10 g·L⁻¹ of S^0 and 100 mg·L⁻¹ of GO. If 100 ml of final suspension was applied into 1 kg of soil, final concentration (in soil) was 1 g·kg⁻¹ of S^0 and 10 mg·kg⁻¹ of GO. Before further dilution, all materials were sonicated twice for 5 min with 2 min break with an ultrasound needle Bandelin Sonopuls HD 2070 homogenizer (Berlin, Germany) using a frequency 20 Hz and then shaken for 24 h at 140 rpm.

Characterization of materials

Scanning electron microscopy (SEM)

The surface characterization of samples was examined by SEM on a Tescan MAIA 3 equipped with a FEG (Tescan Ltd., Brno, Czech Republic). The best images were obtained using the In-lens SE and BSE detectors at working distance between 2.95 and 3.01 mm and at 5 kV acceleration voltage. Images were obtained at 10,000–25,000-fold magnification covering sample area of 8.30–20.80 μ m. Full frame capture was performed in UHresolution mode, and it took about 0.5 min with the \sim 1 μ s/pixel dwell time. Spot size was set at 2.4 nm.

Characterization of size of particles by dynamic light scattering (DLS)

The size of sulfur particles was measured using the Zetasizer Nano ZS instrument (Malvern Instrument Ltd., Worcestershire, UK). The parameters of particle size measurements were as follows: Refractive index of the dispersive phase of 1.957 and 1.333 for the dispersive environment, adsorption coefficient 10⁻³, temperature 25 °C, equilibration time 120 s, and measurement angle of 173° (backscatter). For measurement, disposable cuvettes type DTS0012 (Malvern Panalytical Inc., Westborough, MA, USA) were used, containing 1 mL of samples with concentration 1 g·L⁻¹. Sample of micro- S^0 was 5 min sonicated before measurement.

Atomic force microscopy (AFM)

AFM imaging of the nanostructured surface was carried out using a Bruker Dimension FastScan microscope (Bruker Nano Surfaces, Santa Barbara, CA, USA) operated in PFQNM mode. A triangular silicon nitride cantilever SCANASYST-AIR (Bruker AFM Probes, Camarillo, CA, USA) equipped with a pyramidal silicon tip was used to characterize the surface topography. Cantilever stiffness and sensitivity were calibrated by analysis of thermal noise spectra and were found to be 0.38 N·m⁻¹ and 78.5 nm·V⁻¹, respectively. The following parameters were used to drive the AFM microscope: scanning speed, 0.5 Hz; setpoint force value, 1.25 nN; iGain value, 0.75; and number of points per line, 1500. The raw recorded AFM data were processed in Gwydion software 2.51 [43].

Elemental analysis

All C/H/N/S/O measurements were performed using FLASH 2000 (ThermoFisher Scientific Inc., Waltham, MA, USA) organic elemental analyser. The standards used for measurement were purchased from ThermoFisher Scientific Inc. For CHNS measurement 1–3 mg of measured sample was placed in a soft tin container

and introduced into a quartz reactor filled with copper oxide and electrolytic copper. The reactor was heated to 950 °C and a small volume of oxygen was injected along with the sample. The gases released by the combustion of the sample were measured by the machine's in-built detector. The relative CHNS content was determined by comparing the resulting spectra to a BBOT (2,5-Bis(5-tert-butyl-2-benzo-oxazol-2-yl)) standard. For oxygen measurement the process was analogous. 1–2 mg of the sample was placed in a soft silver container and introduced to a quartz reactor filled with Nickel plated carbon and quartz turnings. The temperature of the reactor was 1080 °C. The oxygen percentage in the sample was determined via comparison to a spectrum of an acetanilide standard.

Pot experiment settings

The 8-week pot experiment with the lettuce seedlings (*Lactuca sativa* L.) was carried out to evaluate the effect of micro- and nanosized amendments (nano-S⁰, micro-S⁰ and GO) on selected soil properties and plant biomass accumulation. The growth substrate was prepared by mixing a silty clay loam (USDA Textural Triangle) Haplic Luvisol (WRB soil classification) taken at field near the town Troubsko (Czech Rep., 49°10'28"N 16°29'32"E) with a fine quartz sand (0.1–1.0 mm; ≥ 95% SiO₂) in a weight ratio of 1:1. The soil properties were as follows: soil macronutrients (g·kg⁻¹)—total C 14.000, total N 1.595, P 0.097, S 0.145, Ca 3.259, Mg 0.236, K 0.231; N forms (mg·kg⁻¹)—N_{mineral} 62.84, N-NO₃ 56.80, N-NH₄ 6.04; pH (CaCl₂) 7.3. One kilogram of this substrate was thoroughly mixed with the amendments given in Table 1 and placed into pot of volume 1 L. All experimental variants were prepared in 4 replications. Experimental pots were placed randomly in a growth chamber (Climacell EVO, BMT, Czech Rep.), where controlled conditions (full-spectrum LED lighting, intensity 370 μmol·m⁻²·s⁻¹; photoperiod 12 h; temperature 18/22 °C night/day; relative humidity 70%) were maintained. Lettuce seeds were sprouted on wet filter paper for 2 days and then five of them were sown to the depth of approximately 2 mm in each pot. After sowing, soil moisture was maintained at

60% of WHC. The 10-day-old seedlings were reduced to only one plant (the most robust) per pot.

At the end of experiment, mixed soil sample was taken from each pot to determine soil properties, and plants were harvested as well. The lettuce seedlings were washed with water, tapped dry, cut apart at hypocotyl to upper part = aboveground biomass (AGB) and lower part = root. Both, AGB and roots, were air-dried at 60 °C to the constant weight in laboratory drier to determine dry AGB and root biomass (AGB_{dry} and Root_{dry}) by weighting on laboratory scales.

Methods for soil properties determination

The following soil properties were evaluated: pH in CaCl₂ [44]; dehydrogenase activity (DHA) [45]; soil basal respiration (BR) and substrate-induced respiration [46]—Glc_SIR (D-glucose), Pro_SIR (protocatechoic acid), Tre_SIR (D-trehalose), NAG_SIR (N-acetyl-β-D-glucosamine), Ala_SIR (L-alanine), Man_SIR (D-mannose); enzyme activities [47]—arylsulfatases (ARS), ureases (Urea), phosphatases (Phos), NAG (N-acetyl-β-D-glucosaminidase), GLU (β-glucosidase).

Statistical analyses

Data obtained from the performed measurements were statistically analyzed using the multivariate analysis of variance (MANOVA), principal component analysis (PCA), one-way analysis of variance (ANOVA), Tukey HSD post-hoc test (at significance level p = 0.05), and Pearson correlation analysis (Program R, version 3.6.1) [48].

Results

Characterization of materials

The purchased nano-S⁰ should exhibit size 47 nm according to the seller. Purchased nano-S⁰ were analyzed using DLS (Fig. 1a) and their measured size was 212 ± 80 nm. The micro-S⁰ exhibited size in the microscale as expected (Fig. 1b).

The morphology of tested materials was studied using SEM. Figure 2a, b shows tested sulfur materials, namely, nano-S⁰ (Fig. 2a) and micro-S⁰ (Fig. 2b). The SEM confirmed the considerably different sizes of nano- and micro-S⁰ and their unspecific shapes. Figure 2c shows GO as a typical large area sheet with fine wrinkles. To confirm the nanostructure of GO the thickness and topography were measured using the AFM (Fig. 3). The line scan profile shows the thickness of GO to 2 nm, in dependence on present functional groups which is in accordance with the literature.

Nanocomposites consisting of GO with nano-S⁰ or micro-S⁰ were successfully synthesized. Figure 4a shows GO densely decorated with nano-S⁰ and Fig. 4b shows

Table 1 Experimental variants

Variant	Amendment and dose
Control	–
GO	10 mg GO·kg ⁻¹ of soil
Micro-S ⁰	1.0 g S·kg ⁻¹ of soil
Micro-S ⁰ + GO	1.0 g S·kg ⁻¹ + 10 mg GO kg ⁻¹ of soil
Nano-S ⁰	1.0 g S·kg ⁻¹ of soil
Nano-S ⁰ + GO	1.0 g S·kg ⁻¹ + 10 mg GO·kg ⁻¹ of soil

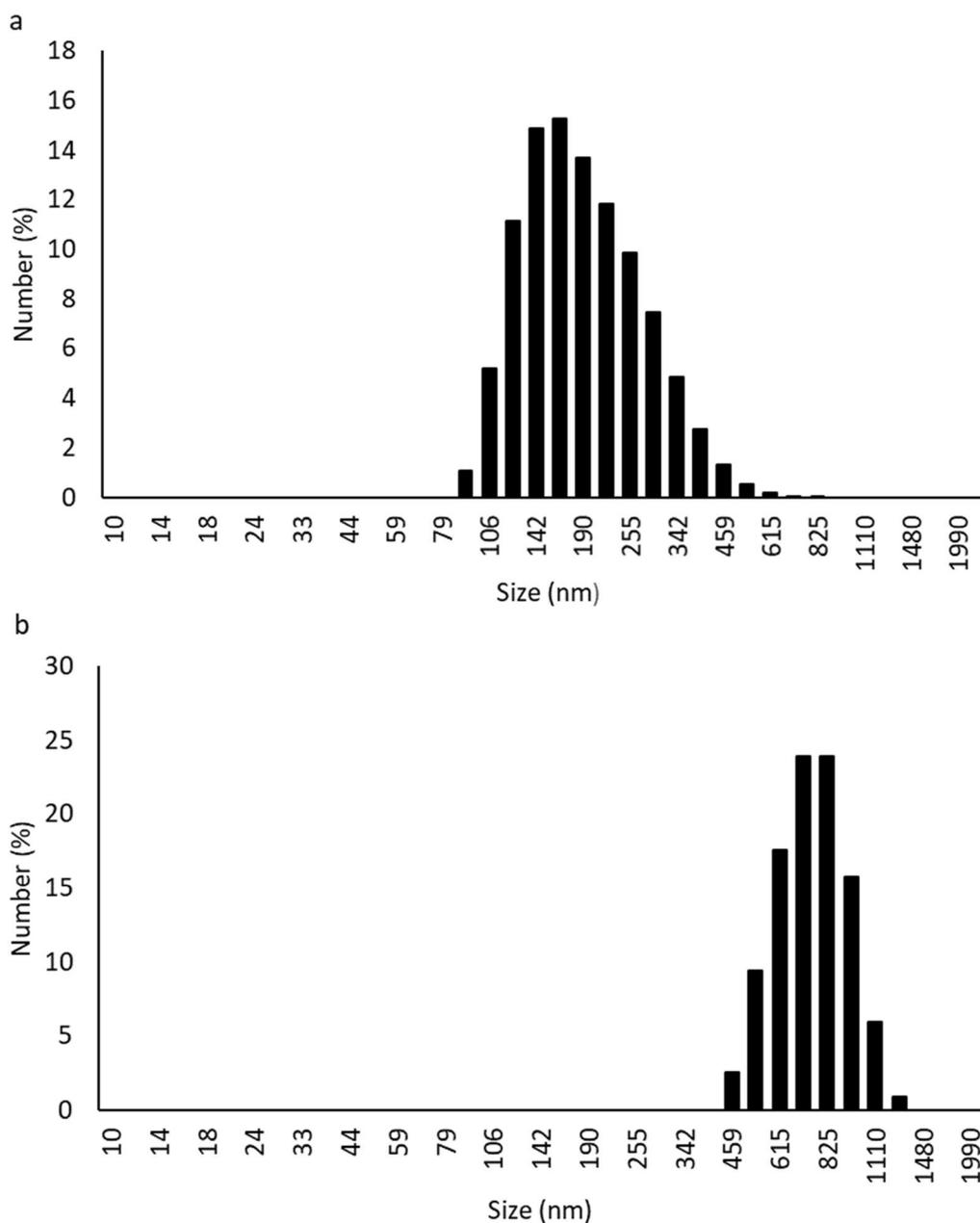


Fig. 1 Dynamic light scattering (DLS) measurement of nano-S⁰ (a) and micro-S⁰ (b) for hydrodynamic size

noticeably larger particles of micro-S⁰ covered with GO. Both images visualized by secondary electrons were also visualized by backscattered electrons and these images are placed next to them. Backscattered electron imaging confirmed the presence of two different materials thanks to their contrast. Sulfur as a heavier element than carbon is shown brighter.

The elemental analysis of GO (Table 2) determined that the sample contains large amounts of carbon and oxygen,

because the carbon grid of GO is constituted by carbon and oxygen is element that constitutes present oxygen-rich functional groups and is accompanied by hydrogen. The high percentage of oxygen indicates a high degree of oxidation which is typical for GO. Any nitrogen was detected in the sample so the column for nitrogen is not mentioned in Table 2. A small amount of sulfur is present probably as a residue of sulfuric acid from the synthesis of GO.

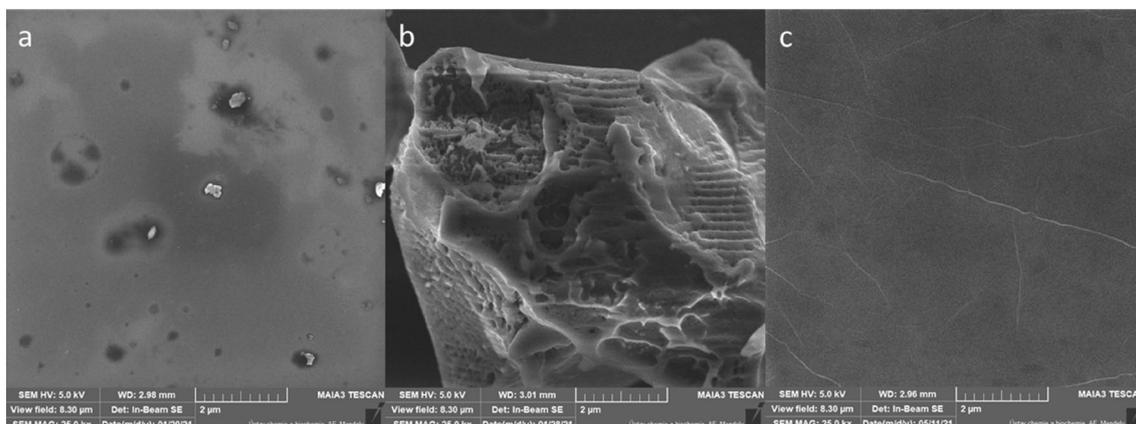


Fig. 2 Scanning electron microscopy (SEM) images of **a** nano-S⁰, **b** micro-S⁰ and **c** GO

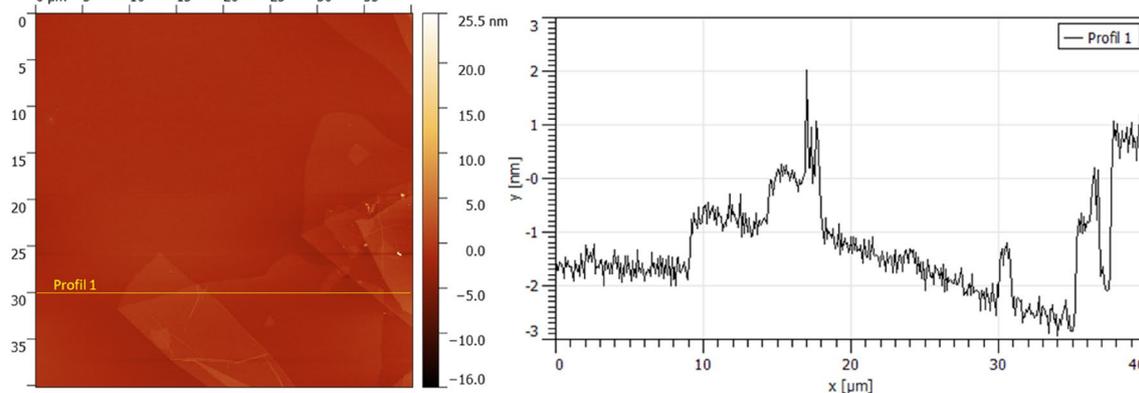


Fig. 3 Atomic force microscopy (AFM) image of GO and the line scan profile

Plant and soil health indicators

Dry root biomass (Root_{dry}) showed only one significant difference among the individual variants and control (Fig. 5a). Nano-S⁰+GO reached the highest value, significantly higher than control. However, dry aboveground biomass (AGB_{dry}) was significantly negatively affected by both micro-S⁰ (with or without GO) and by pure nano-S⁰ (Fig. 5b). On the other hand, the value of AGB_{dry} of nano-S⁰+GO variant was significantly the highest.

Dehydrogenase activity (DHA) was significantly increased in all S⁰-amended variants except of micro-S⁰ and the intercomparison of both variants with S⁰ and both variants with S⁰+GO showed a significant difference due to the particle size of sulfur (Fig. 6a). This shows that nano-S⁰ promoted DHA more than micro-S⁰. On the other hand, GO amendment decrease DHA value.

Also, other determined enzymes showed similar trend. Both arylsulfatase (ARS, Fig. 6b) and N-acetyl-β-D-glucosaminidase (NAG, Fig. 6c) was significantly

increased in all S⁰ amended variants except of micro-S⁰, which putatively did not increase relevant nutrient (S, N) transformation (oxidation). GO addition did not improve effect of variably formulated S⁰ on ARS. GO did not change the values of all enzymes (Fig. 6b–e), except of ARS, which was decreased. On the other hand, other enzyme activities were promoted more by S⁰+GO than by S⁰. In addition, nano-S⁰ significantly improved all enzyme activities compared to micro-S⁰ variant.

Completely opposite to the DHA results were the values of BR and substrate-induced respiration (SIR). BR was significantly decreased in the nano-S⁰-treated variants as compared to the micro-S⁰-treated variants. All amended variants showed significantly decreased D-glucose (Glc-SIR) and protocatechuic acid (Pro-SIR) values in comparison to the control (Fig. 7b, c). A significant adverse effect of nano-S⁰+GO on Glc-SIR, Pro-SIR and D-mannose (Man-SIR, Fig. 7f) induced respiration was found compared with micro-S⁰+GO. Although, this

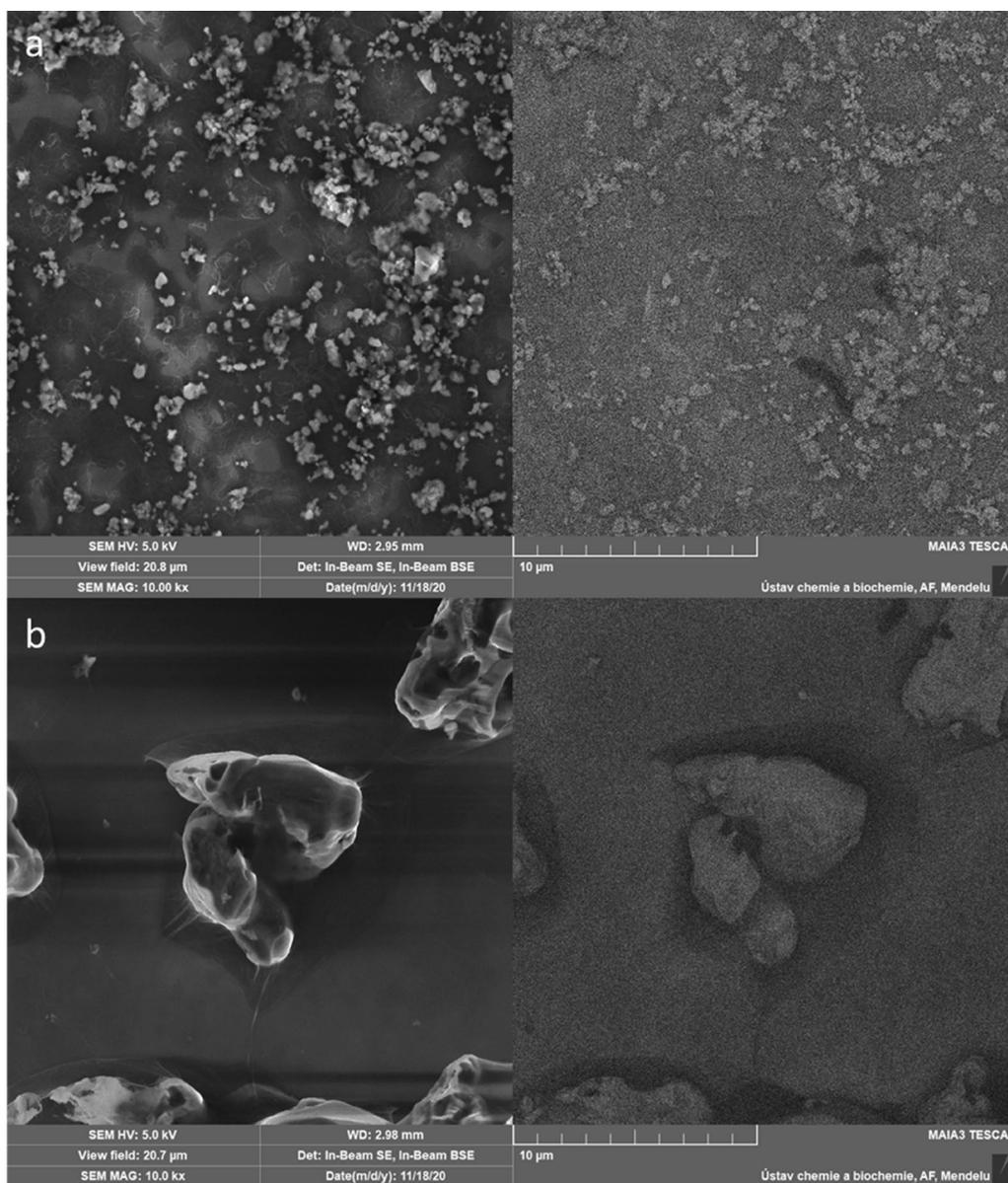


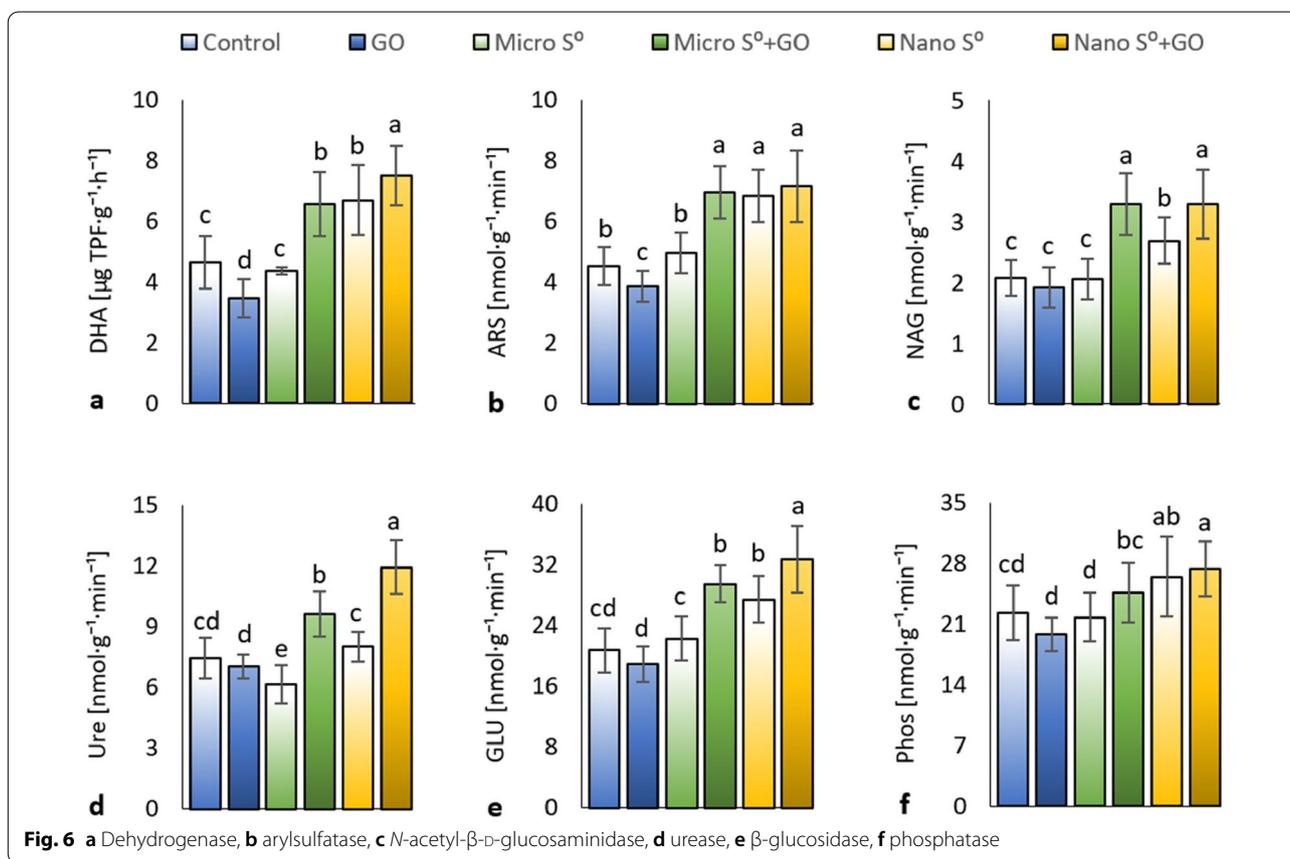
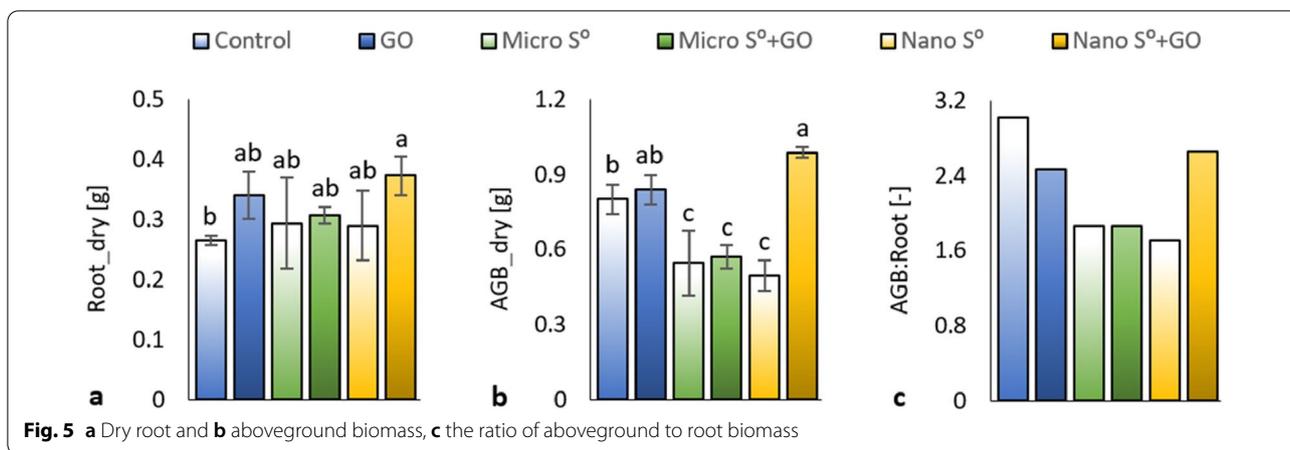
Fig. 4 SEM images of composites **a** GO with nano-S⁰ and **b** GO with micro-S⁰. On the left side are composites visualized by secondary electrons and on the right-side images are visualized by backscattered electrons

Table 2 Elemental analysis (C, H, S, O) of GO

Carbon (%)	Hydrogen (%)	Sulphur (%)	Oxygen (%)
42.23 ± 0.01	2.48 ± 0.15	1.83 ± 0.04	43.56 ± 0.41

effect was not significant between S⁰ variants without GO. There could be observed another trend. Values of BR, D-trehalose (Tre-SIR), N-acetyl-β-D-glucosamine

(NAG-SIR), L-alanine (Ala-SIR), and L-arginine (Arg-SIR) were significantly decreased in the nano-S⁰-treated variants as compared to the micro-S⁰-treated variants (Fig. 6d, e, g, h). The nano-S⁰ + GO amendment significantly decreased all determined types of soil respiration. On the other hand, enrichment of micro-S⁰ with GO led to decrease in the values only of BR, Tre-SIR, NAG-SIR and Ala-SIR. Tre- and NAG-SIR were unchanged without GO and decreased with GO.

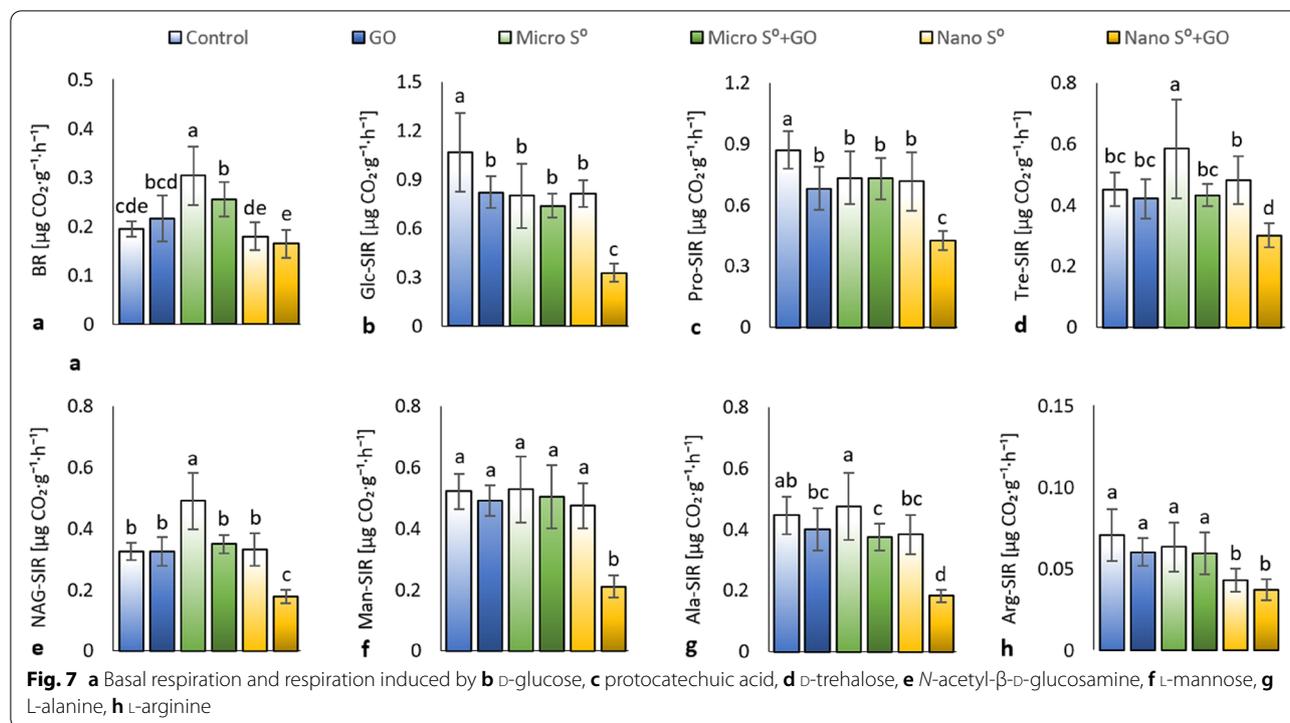


Discussion

Effect of nano- and microsized elemental sulfur on plant biomass and soil properties

At the beginning of the experiment, it was hypothesized that lettuce biomass (both AGB_{dry} and Root_{dry}) would be increased due to improvement of soil

nutrition by the application of S⁰. The root growth and biomass value varied insignificantly for all variants except of control and nano-S⁰ + GO. Moreover, application of pure S⁰ decreased final AGB_{dry} (compared to the control) regardless to the particle size, both micro-S⁰ (with/without GO) and nano-S⁰ exerted adverse impact on the AGB_{dry}. This finding was in contrast



to positive effect of S^0 applied to soil on the reported AGB and root biomass of different crops [49, 50]. It could be due to the different species-specific response of lettuce to S^0 fertilization as it was reported that crop responses to sulfur fertilization may vary from substantial increases to slight reductions in grain yield [51].

Another explanation for the inconsistency with other works may provide the ecotoxicology viewpoint and for this reason, the effects of the amendments on plant health, the ABG_{dry} to $Root_{dry}$ ratios were calculated. This approach was inspired by the root-shoot ratio approach, used frequently in assessment of stress factors on plant growth [52]. In fact, the control sample represents the ratio under non-stressed conditions, and therefore, the results obtained in soil after addition of amendments are compared with this value. The results showed that the most affected plants were by nano- S^0 , micro- S^0 , and micro- S^0 plus GO; the least were affected the plants growing under influence of nano- S^0 plus GO. It is known that the increase of the ratio is caused by favorable growing conditions (except for injury to the roots or other mechanical factors) [52]. Under those conditions, the plants distribute higher proportions of biomass into leaves and stems. A decrease in this ratio indicates that the plant was growing under less favorable conditions, in other words, under stress conditions. In this case, the root biomass increase may result from a completion

for nutrients [53]. As a result, the plants distributed the biomass into growing of roots thereby increasing the surface area for the adsorption of nutrients. As follows from the results and further discussion, in all cases the amendments induced an increased activity of enzymes, which indicates an enhanced activity of microorganisms. As their increased activity requires nutrients, they competed with plants. The nutrient deprivation seems to be decreased in soils amended using GO and GO plus nano- S^0 , where the yields of AGB_{dry} were comparable or higher than control. Previously, the GO-assisted promotion of seed germination, seedling and plant growth has been reported, due to improved hydration, increased root growth, and nutrient supply via increased soil aggregation [54, 55].

DHA, which indicates ability of soil microbiome to degrade soil organic matter (SOM), was stimulated via application of both variants with nano- S^0 (Fig. 6a), but positive effect of micro- S^0 was significant only when co-applied with GO. These results are in the line with reported beneficial effect of low particle size waste S^0 application on soil DHA in the unseeded arable soil [56]. On the contrary, no significant effect of S^0 added to alkaline S-deficient soil was referred, however, at a much lower application dose and unspecified particle size [57]. We ascribe from these findings that effect of S^0 varies depending on the soil properties and interaction with

crop being grown (e.g., lettuce). However, it is obvious that S^0 was beneficial to the degradation microbial activity in soil in the particle size-dependent way, which was agreed with hypothesis I. of the experiment.

DHA correlated significantly ($p \leq 0.001$) positively with all enzymes: ARS, Ure, Phos, NAG, GLU (r was 0.82, 0.66, 0.67, 0.73, 0.77, respectively) Additional file 1: Figure S1. These correlations and synergy displayed by PCA biplot (Additional file 2: Figure S2) indicated that all enzyme activities were closely related and responded to the S^0 amendment with a similar trend. ARS and NAG activities were (in the line with DHA) enhanced by nano- S^0 and but not by micro- S^0 (Fig. 6b, c). Malik et al. [57] also reported that application of S^0 increased ARS activity. The lower effectiveness of micro- S^0 in promoting ARS activity was attributed to a coarser formulation which retarded microbial colonization and transformation of sulfur particles [57]. Moreover, more representative of the genus *Thiobacillus* were found in pasture soil at the fine S^0 than coarse S^0 treatments [5]. Despite the referred antifungal activity of nanosulfur [10, 58], no decrease in the fungal biomass in soil represented by NAG activity involved in chitin degradation was observed. On the contrary, enhanced chitin turnover predicted higher fungal growth in nano- S^0 -amended soil, as fungi are known to contribute to S^0 oxidation [4] and positive response of arbuscular mycorrhizal fungi was reported too [49]. Decreased urease activity in micro- S^0 -treated soil was already discussed above; however, the mitigation of putative inhibition of urease activity in the nano- S^0 -treated soil was detected. β -glucosidase (GLU) and phosphatase (Phos) activities were also positively affected by nano- S^0 amendment in comparison to the effect of micro- S^0 (Fig. 6e, f). This stimulatory effect on GLU and Phos, as well as enhanced labile phosphate availability, due to application of S^0 to soil has been already reported [59]. We attributed these findings to increased microbial abundance, which was also mentioned [57]. All above discussed results of enzyme activities assay confirmed the hypothesis I.

Despite an initial sharp increase in CO_2 production by microbial respiration, this is followed by increased carbon dioxide assimilation as S^0 is oxidized to sulfate [60]. Moreover, highly oxygen-dependent aerobic catabolism of protocatechuic acid may be competed with the oxygen-demanding S^0 utilization. On the other hand, Arg-SIR and Ala-SIR were unaffected with micro- S^0 and decreased by nano- S^0 , and basal respiration, Tre-SIR, and NAG-SIR were enhanced in the variants amended with pure micro- S^0 and unchanged in the nano- S^0 amended ones (Fig. 7). We ascribed from these findings that presumed S^0 -mediated retardation of deamination of highly N-abundant substrates such as L-arginine occurred on

the respiration level as well [61]. Micronized S^0 , rather than nanosized S^0 , showed more significant positive effect of S^0 on the fungal biomass turnover, which was determined at the level of aerobic utilization of the monosaccharide units (D-trehalose, NAG) of fully degraded fungal polymers. Previously it was noted that addition of S^0 to sand fraction of the soil depresses redox potential [62] and may hindered nitrification. Therefore, we assumed that the S^0 -mediated weaker redox potential (E_h), coupled with decreased degradation of amino acids, was attributed to coarser micro- S^0 , whereas generally more interactive finer nano- S^0 could overcome the depressed E_h due to more efficient stimulation of microbial activity. BR correlated significantly ($p \leq 0.001$ and ≤ 0.01 , respectively) negatively with enzymes Ure and Phos (r were -0.42 and -0.32 —Additional file 1: Figure S1) and PCA biplot revealed antagonism of Arg-SIR, Ala-SIR and urease (Additional file 2: Figure S2). All these outcomes denied the validity of hypothesis I. on universally higher enhancement of nutrient conversion derived by nano- S^0 compared to the effect of micronized S. The hypothesis I. was not verified at the level of soil respiration.

Effect of GO (pure) or combined in nanocomposite with S^0 on plant biomass and soil properties

GO was referred by several authors to has an adverse effect on soil microbiome [26, 28, 30]. On the other hand, some positive properties were reported, e.g., improvement in nutrient delivery to plants and the ability to adsorb environmental contaminants [63, 64]. Therefore, we hypothesized that co-application of GO with S^0 would further increase S^0 -mediated transformation rate of SOM, followed by higher lettuce biomass yield. Indeed, we detected significantly higher AGB_{dry} value of nano- S^0 + GO treated variant as compared to other S^0 amended variants (Fig. 5b). We assumed the GO capability to adsorb macro- and micronutrients for improved delivery of nutrients to the soil and plants [63, 65].

GO showed negative impact on DHA and ARS (Figs. 4d, 5a), similar negative impact of GO on soil enzyme activities was referred [29]. This negative feature was suppressed by both, micro- S^0 and nano- S^0 , and all enzyme activities (Fig. 6) were significantly increased in variants micro- S^0 + GO and nano- S^0 + GO as compared to the control. This could be due either to the partial short-term supportive effect of GO on the microbial (fungal) biomass in soil, as referred by [27], or due to the mitigation of GO-mediated reactive oxygen species (ROS) production, which dominantly cause inhibition of basic biological functions of microorganisms [66]. Furthermore, GO-promoted increased access of macro- and micronutrients for microbial growth and activity [63,

65] might also enhance enzyme activity. Based on these results, we confirmed hypothesis II.

GO had negative effect only on Glc-SIR and Pro-SIR, other measured soil respirations did not change compared to the control. This finding was consistent with study [31] which reported non-significantly changed soil respiration when the soil microbiome was exposed to engineered carbonaceous nanomaterials. Combined effect of GO + S⁰, mainly in nanosize, on soil respiration was negative (Fig. 7). Micro-S⁰ + GO decreased BR, Tre-SIR, NAG-SIR, and Ala-SIR as compared to the variant with pure micro-S⁰. The negative effect of nano-S⁰ + GO was significant (compared to nano-S⁰ and control) in all substrate-induced respiration, except of Arg-SIR. We predicted coupled strong negative effect of enhanced sulfur oxidation in nano-S⁰ + GO treated soil. The reason could be both competition of S⁰ oxidation with organic carbon oxidation, and changes in activity of enzymes which catalyze oxidation of degradable carbonaceous compounds in SOM. This similar feature was reported for lignin and lignin model compounds (LMCs) [67]. We considered this adverse effect of GO in combination with S⁰ to be more significant for nano-S⁰ + GO than micro-S⁰ + GO variant, since pure nano-S⁰ showed significant adverse on more types of soil respiration.

These observations did not support the hypothesis II. about GO-derived increase in S⁰-mediated carbon transformation rate of SOM.

Conclusions

The results showed that S⁰ of different sizes, applied alone or with GO, showed a significant benefit of nanosized S⁰, which improved most of enzyme activities (dehydrogenase, arylsulfatase, *N*-acetyl- β -D-glucosaminidase, β -glucosidase, phosphatase). However, respirations induced by D-glucose, protocatechuic acid, L-arginine were decreased. The positive effect was hypothesized as well as desirable GO-derived mitigation of negative to neutral effect of micro-S⁰ in dehydrogenase and urease activity. Micro-S⁰ was further found beneficial for BR and respirations induced by D-trehalose and *N*-acetyl- β -D-glucosamine. As expected, nano-S⁰ + GO improved plant biomass yield and enzyme activities. However, nano-S⁰ + GO significantly decreased all substrate-induced respirations. The benefit of soil amendment of nano-/micro-sized elemental sulfur and its combination with nanocarbon (GO) to the soil biologic parameters was partially proven.

Abbreviations

AGB: Aboveground biomass; ANOVA: One-way analysis of variance; Arg-SIR: Respiration induced by L-arginine; ARS: Arylsulfatase; BR: Basal respiration; DLS: Dynamic light scattering; DHA: Dehydrogenase activity; Glc-SIR: Respiration

induced by D-glucose; GLU: β -Glucosidase; GO: Graphene oxide; NAG: *N*-Acetyl- β -D-glucosaminidase; NAG-SIR: Respiration induced by *N*-acetyl- β -D-glucosamine; PCA: Principal component analysis; Phos: Phosphatase; Pro_SIR: Protocatechuic acid; S⁰: Elemental sulfur; SD: Standard deviation; SEM: Scanning electron microscopy; SIR: Substrate-induced respiration; Tre-SIR: Respiration induced by D-trehalose; Urea: Urease.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40538-022-00323-1>.

Additional file 1. Fig. S1 Pearson's correlation matrix of results from plant and soil properties determination. The stars indicate a level of significance in statistical difference between the variables: * for $p \leq 0.05$, ** for $p \leq 0.01$, *** for $p \leq 0.001$.

Additional file 2. Fig. S2 PCA biplot analyses of results from plant and soil properties determination Research.

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Author contributions

TH was involved in conceptualization, data curation, writing—original draft. JH was involved in data curation, investigation, writing—review and editing. DH was involved in software and methodology. AK was involved in formal analysis, investigation, and software. PS was involved in conceptualization, methodology, writing—review and editing. ZB was involved in Software, writing—review and editing. JP was involved in data curation, software. JK was involved in formal analysis, funding acquisition, supervision, writing—review and editing. AM was involved in formal analysis, writing—review and editing. MR was involved in validation, writing—review and editing. OM was involved in data curation and validation. LV was involved in formal analysis and investigation. MB was involved in conceptualization, formal analysis, funding acquisition, supervision, writing—review and editing. All author read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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