Multiphysical analysis of nanoparticles and their effects on plants

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Abstract

Nanoparticles are the magic bullets and at the leading edge in the field of nanotechnology because of their unique properties make these materials indispensable and superior in many areas such as electronic. Extensive applications of nanomaterials incontrovertibly entering our living system. The increasing use of nanomaterials into the ecosystem in one of the crucial environmental factors that human is facing. Nanomaterials raise noticeable toxicological concerns particularly their accumulation in plants and the resultant toxicity may affect the food chain. Here we analyzed the characterization of nanomaterials such as graphene, Al_2O_3, TiO_2, and SiC. Quantitative evaluation of the nanomaterials was conducted and discussed on their commercialization aspects. Various characterization techniques SEM, XRD, UV were utilized to identify the morphology, phase, absorbance, and crystallinity. In addition, we analyze the effects of nanomaterials on plants. The toxicity of nanoparticles has severe effects on loss of morphology of the plants. Potential mechanisms include physical effects, physiological effects were analyzed. In the future study, it is indispensable to assess widely accepted toxicity evaluation for safe production and use of nanomaterials.

Keywords: Nanoparticles, Multiphysical, Plants, Toxicity, Morphology, UV, XRD

Highlights

1. Characteristics of nanomaterials including morphology and crystallinity have been presented
2. Quantitative evaluation and discussion of the nanoparticles on their commercialization aspects
3. Impact of nanoparticles on plants has been discussed
4. Potential mechanisms include physical effects, morphological effects were analyzed

1. Introduction

Nanosized materials present properties different from their bulk embodiment. Their exponential increase of the reactivity at the molecular level due to their high surface to volume ratio. Chemical properties, optical, electrical, and electronic properties need to be considered while the mechanical properties may also differ widely. It is also essential to know the environmental risk assessments of different engineered nanoparticles with the help of the characterization of nanoparticles and their accumulations [1-4]. The new era of science is created in the production of nanoparticles by the development of technologies. Nanoparticles are bridging the gap between bulk materials and atomic or molecular structures as the consequence they have a great scientific interest. Today, the range of elements and compounds successfully synthesized in nanometer-scale forms, characterized, and even deployed as commercial products including metals, metal oxides, polymers, semiconductors, and carbon compounds. The nanometer-scale forms exhibit quantum effects, lower melting temperatures, increased catalytic activity, and faster rates of reaction. Synthesizing nanoparticles is energy-intensive to current chemical methods; producing outdated toxic chemicals, with the high cost and inefficient. Nanoparticle synthesis is substantially lower cost in biological methods that would help to synthesis at mild pH, pressure and temperature. Either intracellular or extracellular, many microorganisms can provide inorganic materials depending on the area where the nanoparticles or nanostructures are produced. In the presence of enzymes, the microbial cell to form the nanoparticles when the intracellular method consists of transporting ions. In the presence of enzymes, the metal ions on the surface of the cells are trapped by the involvement of the extracellular synthesis of nanoparticle that also reduces ions. Out of these two possible methods, the purification process has easy to establish in case of extracellular synthesis of metal nanoparticles is of greater commercial applications. So far, many microbes such as magneto tactic bacteria, diatoms, S-layer bacteria, fungi, actinomycete and yeast are used to generate nanostructured mineral crystals and metallic nanoparticles. Nanometer-scale metal oxides have been intensely investigated over the last few decades. Metals, metal oxides at the nanometer scale behave differently from their macroscopic forms. The members of the group of metal oxides consisting of Al_2O_3, TiO_2, ZnO, and Fe oxides all have interesting properties, which can be exploited in a number of nanotechnology-based applications. Alumina is used in implants which is one of the inert biomaterials. And also, a biodegradable material, that is well tolerated by the biological environment [5]. High biocompatibility and excellent corrosion resistance behaviors can be suggested by TiO_2 [6]. Many undesired organic pollutants are mineralized through TiO_2 [7]. Among the other nanoparticles, the peculiar attributes of graphene [8] have devoted an extensive scientific amenity and have increased high anticipation for its uncovered implementations both in the field of electronics, photonics, composite materials, and energy generation and storage, also in biological fields [9-12]. On mammalian cells, microcrystalline SiC has been utilized for studying the impact of SiC [13]. It has been noticed that micro SiC does not create any initial pestilential impacts on tissues [14]. Graphene grown on SiC is of special behavior because of the chance to neglect to transfer of free stable graphene to a wished substrate while achieving a major area SiC (semi-insulating or conducting) substrate prepare for device processing [15]. Greater agricultural sustainability can be achieved by the contribution of nanotechnology [16] and has noticeable attention due to its potential for use in a wide range of applications [17]. It can be used to minimize the intentness of agrochemicals that are provided in the field, while at the same time quality and productivity of crops are enhancing [16]. Due to the advanced properties, they are attractive candidates for different commercial and domestic applications, which include catalysis, medical applications, energy-based research, imaging, and environmental applications. This paper provides a detailed overview of the characteristics, impact, environmental effect performance and appeals of nanoparticles (NPs) exist in several appearances.

2. Methodology

2.1 Nanoparticles elaboration and characterization methods

For the characterization of nanoparticles, size and shape are discussed predominantly among the other parameters. Organic ligands present on the surface of the nanoparticles may affect possible applications of the nanoparticles. In addition to that crystal structure and their chemical compositions are rigorously analyzed after synthesizing nanoparticles. Robust and credible analysis techniques for nanoparticles will immensely affect in consideration of these nanomaterials in industrial applications. However, the characterization of nanoparticles is of significant challenges due to its interdisciplinary nature. Figure 1 shows the characterization techniques of the nanoparticles (NPs) in the present study.

The morphology characterization of NPs is becoming a crucial task at modern high-resolution SEM microscope and it is a most widespread morphology analytical instruments prescript to characterize physical properties such as morphology, the size distribution of materials at the nano or micro levels, and shape. The crystal structure of NPs needs to be thoroughly characterized and X-ray diffraction (XRD) is the most broadly used tools for the characterization of NPs. Usually, XRD provides information regarding the crystalline grain size, crystalline structure, lattice parameters, and nature of the phase. The latter parameter is calculated by utilizing the Scherrer equation using the most intense peak of an XRD graph. The composition of materials can be investigated by comparing the intensity and position of the peaks with the reference pattern available from the International Centre for diffraction data (ICDD) database. UV-Vis spectroscopy is another comparatively low cost and facile characterization technique that is extensively used to characterize the nanoscale materials. Nanomaterials have the optical properties that are sensitive to shape, size, concentration, agglomeration, refractive index near the surface of the nanomaterials which make UV-Vis spectroscopy a crucial technique to investigate and characterize the materials and evaluate the stability of nanomaterials.

2.2 Soil preparation and experimentation

The soil was collected from the field at DUET (24°01'07.6"N 90°25'03.0"E). The properties of soil are 6.20 P^H, moisture content 24%, organic carbon 5.6% and organic matter 9.5%. 100 g weight soil clay with the respective P^H soil was adopted to the test container and 5 g of each NPs Al_2O_3, graphene, TiO_2, and SiO_2 was spiked with the soil as shown in Figure 2. The effects of the NPs investigated for the *Jasminum multiflorum* and compared the effects without spiked NPs. After spiking water was added to the soil container to maintain moisture content. Soil with plants was incubated for 14 days and stored at 28 °C. After 14 days various effects were analyzed.

3. Results and Discussion

3.1 Characterization of Al_2O_3 NPs

Al_2O_3 NPs reveal predominant metastable polymorphic phases such as alpha (α), gamma (γ), delta (δ) and theta (θ) forms [18]. However, phase metamorphosis of Al_2O_3 may be affected by several parameters such as particle diameter, contaminations and calcination rate [19].

The morphology of Al_2O_3 NPs is shown in Figure 3(a). From the SEM image of Al_2O_3 NPs, it is obvious that nanoparticles are agglomerated in nature. SEM analysis of Al_2O_3 NPs revealed the homogeneous spherical shape and randomly distributed grains. The UV-vis spectra of Al2O3 NPs are shown in Figure 3(b). From the UV-vis spectra graph, it is seen that absorbance band at 292 nm [20], this is maybe excitation of electrons from the valance to the conduction band [21]. Figure 3(c) confirms that the broadband reflectivity alleviation over the whole 200-1100 nm spectral range for Al2O3 NPs. XRD pattern of Al2O3 NPs is shown in Figure 3(d). The presence peaks at 2θ corresponding to (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (0 1 8), (2 1 4), (3 0 0), (1 0 1) diffraction planes confirmed the formation of rhombohedral structure (JCPDS 88-0826) [22]. The presence of intensity peaks at different 2θ is indicated the crystalline nature of Al_2O_3 NPs as well as α-Al2O3 NPs [23].

3.2 Characterization of SiC NPs

Owing to SiC superior mechanical properties, excellent chemical stability, oxidation resistance even at high temperature, good thermal conductivity, and large bandgap which enables SiC NPs application in nanodevices, composites reinforcements, heat exchanger, optoelectronics [24]. The morphology of SiC NPs is shown in Figure 4(a). From the SEM image of SiC NPs, it is showed fairly homogenous cubic shape NPs and average particle size is 4 nm. The UV-vis spectra of SiC NPs are shown in Figure 4(b) and 4(c). From the UV-vis spectra figure, it can be seen that absorption of SiC NPs lies in the UV region. However, no absorption is seen in the visible region and the absorption band is found at 342 nm. From the XRD patterns shown in Figure 4(d), major diffraction peaks attributed at different 2θ corresponding to (1 0 1), (1 1 1), (2 0 0), (2 2 0), (3 1 1) are in a good agreement with the standard values of β-SiC and lattice plane of β-SiC and crystalline size found to be 18nm. The low-intensity peak at a lower diffraction angle than that of the strong (1 1 1) peak is marked as the presence of stacking faults and Hu et al. [24] are studied similar phenomena.

3.3 Characterization of multilayer graphene NPs

Graphene is the most rigorously studied material due to its wide range of applications including energy, electronic, and sensors. Moreover, because of the unique physical and chemical properties of graphene nanomaterials have drawn increasing interest, and, conceivably, apprehended the greatest pledge for implementation into a wide range of bio-applications [25]. Consequently, the graphene NPs hybrid structure offers unique physicochemical properties that are beneficial for bioapplications. The morphology of the graphene NPs is shown in Figure 5(a). From the SEM image of the graphene NPs, layered type structure is observed. In addition, some agglomerated sheets, crumpled nanosheet, and some small sheets which are overlapped and randomly arranged with each other. The UV viz transmittance spectra were estimated wavelength of around 260nm shown in Figure 5(b). The interlayer spacing structure of graphene determined by sharp peaks cited corresponding to the plane (0 0 2) (JCPDS card 05–068) as shown in Figure 5(d).

3.4 Characterization of TiO_2 NPs

TiO_2 NPs is considered the most widely used oxide in photocatalysis [27]. TiO_2 NPs has distinctive characteristics such as non-toxic, favorable band edge positions, low fabrication cost as well as diverse morphological characteristics [28]. The morphology of TiO_2 NPs is shown in Figure 6(a). From the SEM image, it is seen that dense agglomeration of NPs and was irregular shapes. The sharp peaks 360 nm indicating bipyramidal structure formation of TiO_2 NPs as shown in Figures 6(b) and 6(c). The shape and size of the NPs qualitatively analyzed by the shape and peak position. The particles size of nanomaterials associated diffraction peak amplifying. Thus, XRD spectra of the TiO_2 NPs were analyzed and phase size and phase composition were calculated. Figure 6(d) shows the XRD peaks of the TiO_2 NPs. The nanocrystalline bipyramidal structure was determined by sharp peaks cited corresponding to the planes (1 1 0), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 0), (2 2 0) and (2 2 4) belongs to the bipyramidal structure of TiO_2 NPs. All peaks confirmed were in good agreement with the JCPDS database (89–4921). The sharp diffraction peaks reveal that the NPs are crystalline and pure and the NPs were privileged oriented with (1 1 0) face. The sharp diffraction peaks and the values of full width at half maximum reveal that the synthesized nanoparticles are pure and crystalline. The average crystalline size calculated using the Debye–Scherrer formula is found to be 18 nm. This result reveals that the synthesized TiO2 nanoparticles were preferentially oriented with (101) face and crystalline size found to be 20 nm.

3.5 Effects of nanomaterials on plants

3.5.1 Effects of Graphene NPs on plants

The general impact of GFNs on plant development is portion subordinate. Graphene at 5 mg/L advanced the number of unusual roots, and expanded the root and shoot a crisp load of rice seedlings; be that as it may, at centralization of 50 mg/L, it altogether repressed the stem length and new shoot weight [29]. Graphene at 500 mg/L brought about just a slight reduction in root and shoot length of tomato, cabbage, and red spinach, while a stamped restraint was instigated by graphene at fixations up to 2,000 mg/L [30]. Anjum et al. [31] found that GO at 1600, 200, and 100 mg/L altogether restrained the germination rate and root length of the faba bean (Vicia faba), while the wellbeing status of the plant was improved with the presentation to GO at 400 and 800 mg/L. Their past examination evaluated the resilience of faba bean to GO, in which the plant demonstrated a fundamentally higher affectability to GO at 1,600, 200, and 100 mg/L, and its resistance expanded when presented to 400 and 800 mg/L fixations [32]. The following Figure 7 shows the depiction of the phytotoxicity of the graphene nanomaterials (GFNs). The principle of physical systems for the phytotoxicity of GFNs incorporate the concealing impact, mechanical damage, and physical blockage. Both concealing impact and mechanical damage are seen in Figure 8. It is observed that the scattered and obscured GFNs diminished light around 16% of development restraint and direct entrance into algal cells by graphene materials. The physical blockage is firmly identified with the size of GFNs as shown in Figure 8. The graphene NPs has greatly influenced plants delayed germination of seedlings, fresh weight, and root volume stem length [33]. Graphene sheets hinder plants translocation from the roots to the leaves bioaccumulation was lower. Based on physicochemical properties graphene could absorb micronutrients (Mg, N, Ca, P) from the cultural medium leading indirect toxicity [34].

NPs aggregated at the root surfaces and surface layers, hence diminishing the water driven conductivity and take-up of supplements [35]. In this regard, diminishing the accessible light required to help plant development. The physical blockage is firmly identified with the size of GFNs.

3.5.2 Effects of TiO_2 NPs on plants

TiO_2 NPs show an expansion in nitrate re-teaches in Soybean (Glycine max), upgrade the capacity to retain water. TiO_2 NPs treated seeds delivered plants that have 73% progressively dry weight, higher photosynthetic rates, and 45% ascent in chlorophyll a development contrasted with the power over the germination time of 30 days [36]. The development pace of spinach seeds, despite what might be expected, is corresponding to the size of the materials, demonstrating that the littler the nanomaterials, the better the germination. A few examinations guaranteed that the TiO_2 nanoparticles may have raised the ingestion of inorganic supplements quickened the breakdown of natural substances, and caused extinguishing by oxygen free radicals shaped during the photosynthetic procedure, therefore improving the photosynthetic rate [37, 38]. In the meantime, TiO_2, in the anatase stage, builds plant development in spinach by improving nitrogen digestion that advances the adsorption of nitrate [39]. The effects on the morphology of the plants due to TiO_2 NPs are shown in Figure 9. Growth of the plants was negatively affected by the concentration of TiO_2 NPs during 14 days of experimentation. The consistency of previous studies which investigated growth reduction in *Spirodela polyrrhiza* plant treatment of TiO_2 NPs [40]. For spinach seeds, TiO_2 nanoparticles helped water retention, and thus quickened seed germination [37]. It is demonstrated that a mix of nanosized TiO_2 could improve the nitrate reductase protein in soybean (Glycine max), increment its capacities of engrossing and using manure and water, energize its cancer prevention agent framework, and hurry its germination and development [41]. However, it is expressed that the beneficial outcomes of TiO_2 could be investigated because of antimicrobial properties of nanomaterials which can improve the quality and opposition of plants to pressure.

Be that as it may, the nearness of TiO_2 emphatically impacts the plants' development. For instance, TiO_2 nanoparticles were seen to advance the development of spinach through improvement in nitrogen digestion and photosynthetic rate. In addition, Photocatalyzed properties TiO_2 NPs enhance the light absorbance and transmission and induced carbon dioxide assimilation [42].

3.5.3 Effects Al_2O_3 NPs on Plants

Phytotoxicity of uncoated and phenanthrene-covered alumina (Al_2O_3) nanoparticles demonstrated that uncoated Al_2O_3 nanoparticles at 2 mgL^{-1} fixations repressed the root lengthening of cucumber, corn, carrot, cabbage, and soybean [43]. It is referenced that the lethal impact is most likely not nano specified because of the disintegration of Al_2O_3 NPs. The impacts of submicron Al_2O_3 particles were explored to assess the concoction material that may be dangerous towards the development of seedling roots [44]. In this way, molecule surface attributes assume a basic job in the phytotoxicity of Al_2O_3 nanoparticles [45]. Figure 10 shows the effects and morphological loss due to toxicity of Al_2O_3 NPs on plants. It is observed, after 14 days Al_2O_3 NPs affect the number of leaves and *Jasminum multiflorum*. We also observed that the concentration of Al_2O_3 NPs increased the biomass. Similar phenomena were observed for *Nicotiana tabacum* with Al_2O_3 NPs concentration [46]. However, the nearness of Al_2O_3 nanoparticles didn't negatively affect the development of Lolium perenne and Phaseolus vulgaris in the tried fixation run [47]. Al_2O_3 nanoparticles focus in ryegrass improved the control investigation by 2.5 occasions, with no take-up, was seen in kidney beans, which surmised the distinction in the take-up and dispersion proficiency of various plants by comparative nanoparticles [48].

3.5.4 Effects of SiC NPs on plants

The reaction of plants to nanoparticles relies upon different variables, including the size, shape, technique for application, synthetic properties, and physical properties of the nanoparticles [49]. This investigation has indicated that SiC NPs may straightforwardly communicate with plants and affect their morphology and physiology as shown in Figure 11 in different manners, including the expansion of auxiliary shading to the plants, and help in improving plant development and yield [50]. However, after 14 days of experimentation, some physical damage, membrane damage, leaves growth were identified. A few examinations have additionally demonstrated a negative effect of SiC NPs on plants [51, 52, 53]. In many investigations, Si-NPs were seen to be advantageous to or incapable for plants by either supporting plant development or not affect [50] except a couple of reports where Si-NPs were seen to negatively affect plants [54]. Slomberg et al. [55] revealed that the dangerous effect of Sic NPs was because of the adjustment in p^H in development media that happened because of the expansion of Si-NPs.

4. Conclusion

This comprehensive study on NPs characterizations demonstrates the use of NPs, advantages and limitations. The acquisition of a variety of full picture of the NPs features discussed through the various analysis methods.

Al_2O_3 NPs shows agglomerated in nature and homogeneous spherical shape, and absorbance band at 292 nm. XRD analysis of Al_2O_3 NPs reveals the crystalline nature of Al_2O_3 NPs and α-Al2O3 NPs. SiC NPs exhibits homogeneous cubic shape and average particles size 4 nm, and absorption band at 342 nm. In addition, the crystalline size of SiC NPs represents β-SiC and lattice plane of β-SiC. It can be concluded that SiC NPs have high purity in accordance with the results. TiO_2 NPs shows agglomeration, irregular shapes, and absorbance peaks at 360 nm indicates the bipyramidal structure. The monocrystalline bipyramidal structure was determined using XRD analysis and crystalline size is found to be 18 nm. It can be concluded that TiO_2 NPs could be a substituent for gate dielectric application [56]. In the case of graphene NPs, graphene NPs shows immense potential due to its intrinsic physical, chemical, morphological, absorbance, and mechanical properties. The prospects of graphene NPs is very bright with control shapes, sizes, crystallinity, composition, morphology, low defects as well as high yield manner. This study shows, graphene NPs have some agglomerated sheets, crumpled nanosheets, and some small sheets which are overlapped and randomly arranged with each other and XRD results show interlayer spacing. This hybrid structure of graphene NPs can e applied to a wide variety of bioapplications [26].

Effects of NPs on plants, Plant toxicity, the physicochemical properties of NPs, bioassay are crucial factors in toxicity evaluation. At present, competitive toxicity analysis between nanoparticles has been carried out for lower plant forms. The common toxicity indications observed in plants exposed to NPs are an acute loss of morphology.

Further risk evaluation in a large of plants must be methodically investigated. At present, plant germination, physiology, growth are used to assess the toxicity of NPs in most studies. However, these indicators might not fully reflect the toxic effects and mechanisms of NPs. Compared to analyzing of NPs toxicity, distribution, the uptake, and degradation of NPs within plants remain poorly visualized [57]. Present research shows, NPs are in use into the environment should be avoided to the large scale possible. For this contemplate, the cooperation of biologist and chemists is essential to implement accurate preventive management strategies for safe production and use.

Conflict of Interest: The authors declare that there is no conflict of interest.

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Figure Legends

Figure 1: Multi-physical analysis techniques of nanoparticles in present study

Figure 2: Experimentation of uptake and translocation of the NPs in plants

Figure 3: Characterization of Al_2O_3 NPs, (a) SEM image, (b) UV-viz absorption spectra, (c) UV-viz transmittance spectra and (d) XRD pattern of Al_2O_3 NPs.

Figure 4: Characterization of SiC NPs, (a) SEM image, (b) UV-viz absorption spectra, (c) UV-viz transmittance spectra, and (d) XRD pattern of SiC NPs

Figure 5: Characterization of multilayer Graphene NPs, (a) SEM image, (b) UV-vis absorption spectra, (c) Depicted graphene nanosheet and (d) XRD pattern of Graphene NPs.

Figure 6: Characterization of TiO_2 NPs, (a) SEM image, (b) UV-viz absorption spectra, (c) UV-viz transmittance spectra, and (d) XRD pattern of TiO_2 NPs.

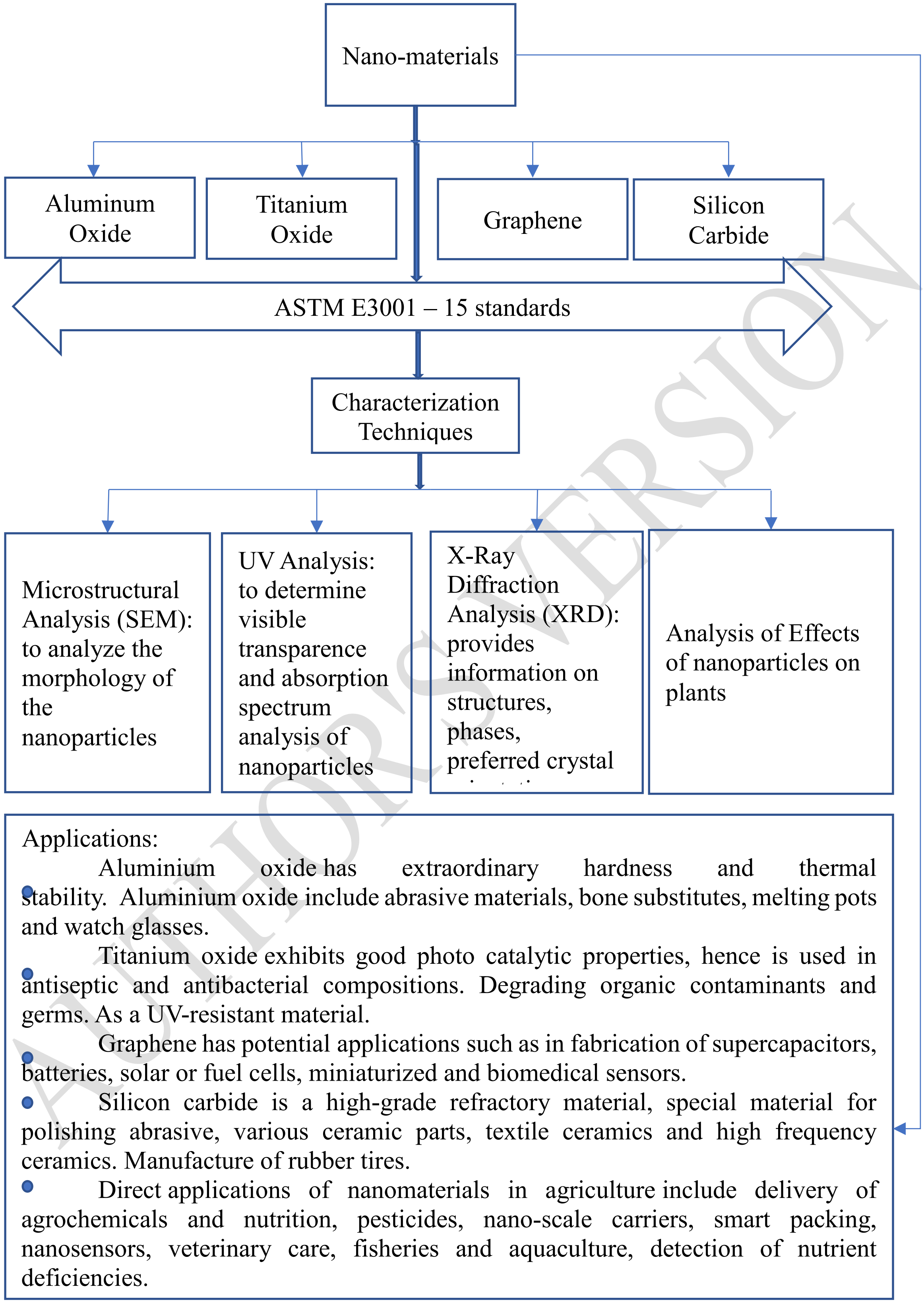
Figure 7: Depiction of the phytotoxicity of GFNs

Figure 8: Observation of effects of graphene NPs on plants (a) tree inside graphene aqua solution (b) tree inside graphene aqua solution after 2 weeks (c) stem and leaf condition after 2 weeks (d) SEM image of stem (e) SEM image of green leaf (f) SEM image of yellow leaf

Figure 9: Observation of effects of TiO_2 NPs on plants (a) tree inside TiO_2 aqua solution (b) tree inside TiO_2 solution after 2 weeks (c) stem and leaf condition after 2 weeks (d) SEM image of stem (e) SEM image of green leaf (f) SEM image of yellow leaf

Figure 10: Observation of effects Al_2O_3 NPs on plants (a) tree inside Al_2O_3 aqua solution (b) tree inside Al_2O_3 aqua solution after 2 weeks (c) stem and leaf condition after 2 weeks (d) SEM image of stem (e) SEM image of green leaf (f) SEM image of yellow leaf

Figure 11: Observation of effects of SiC NPs on plants (a) tree inside SiC aqua solution (b) tree inside SiC aqua solution after 2 weeks (c) stem and leaf condition after 2 weeks (d) SEM image of stem (e) SEM image of green leaf (f) SEM image of yellow leaf



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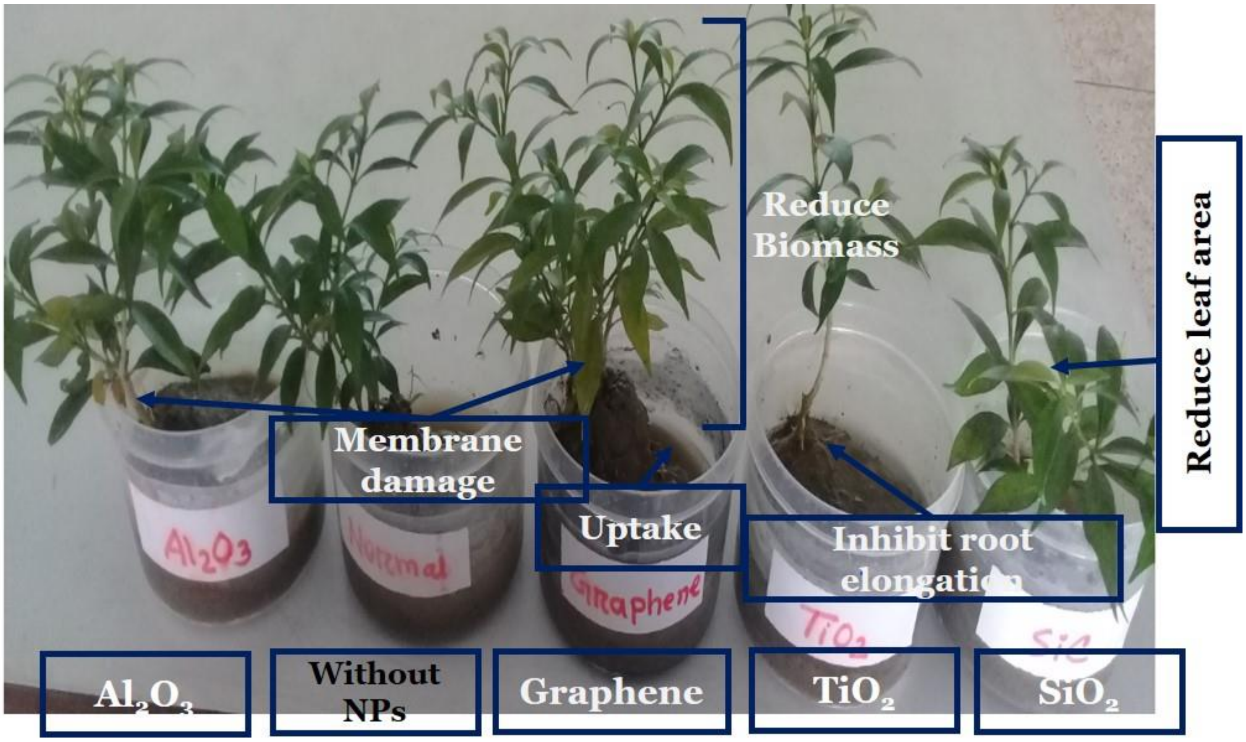

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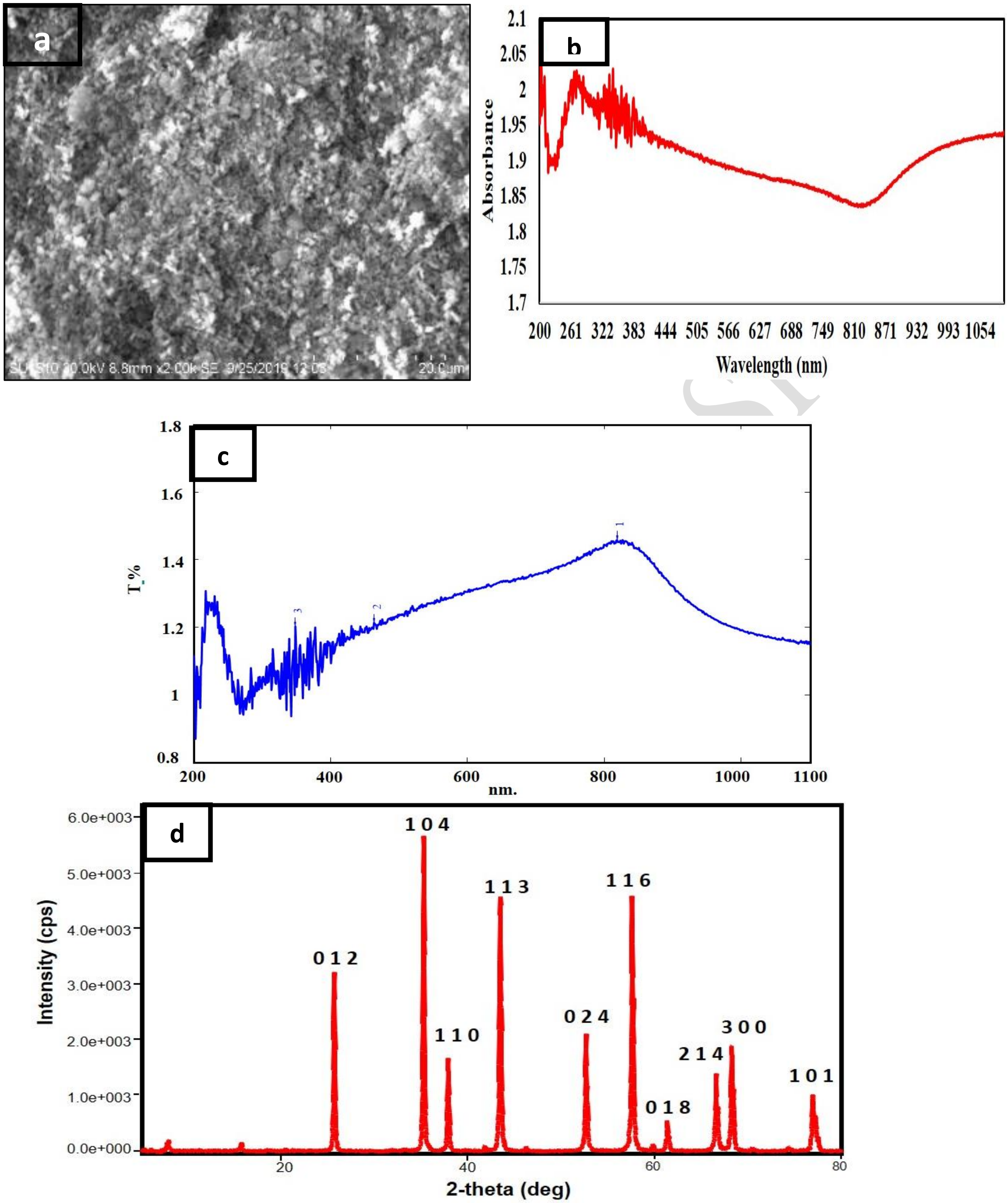

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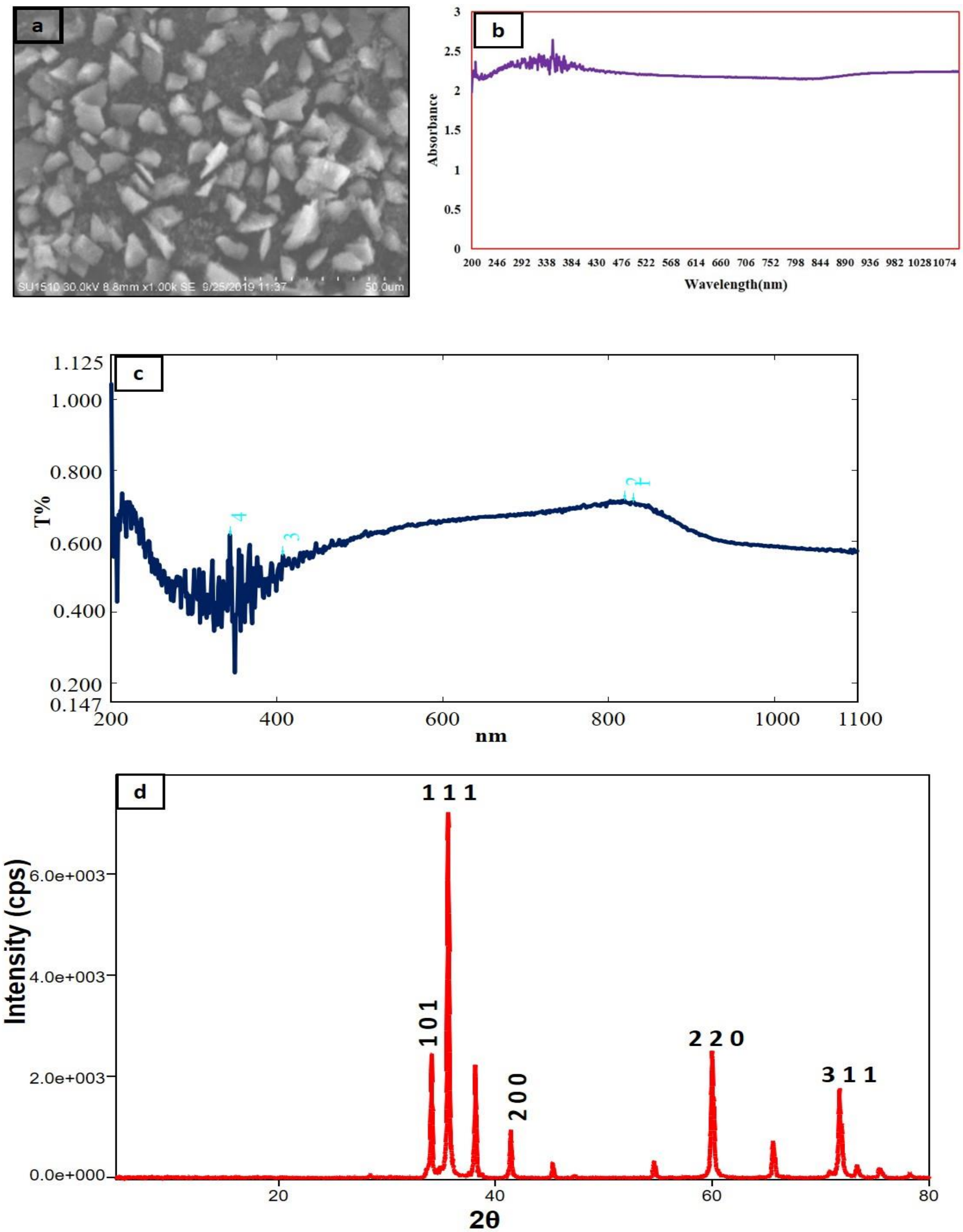

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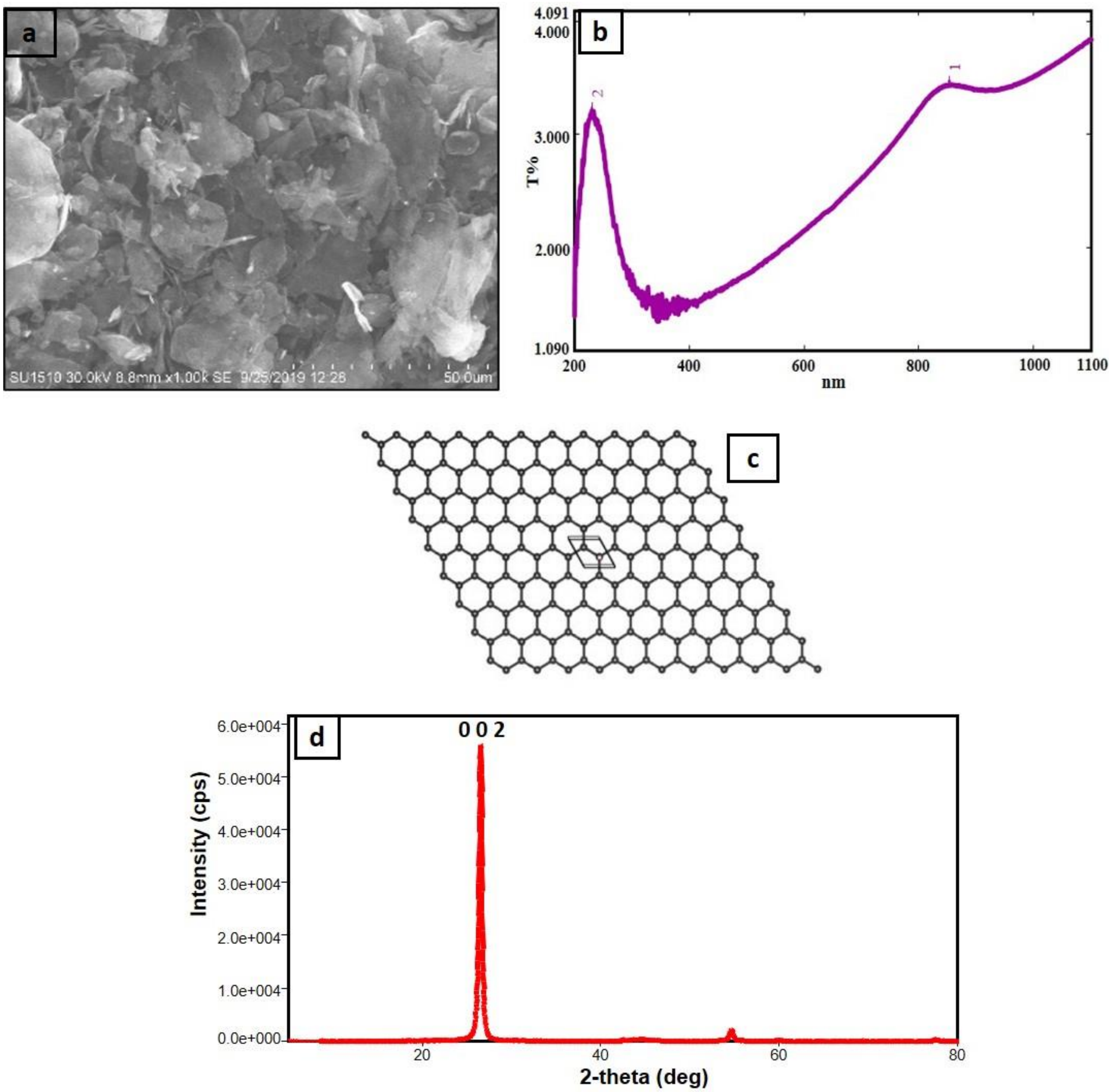

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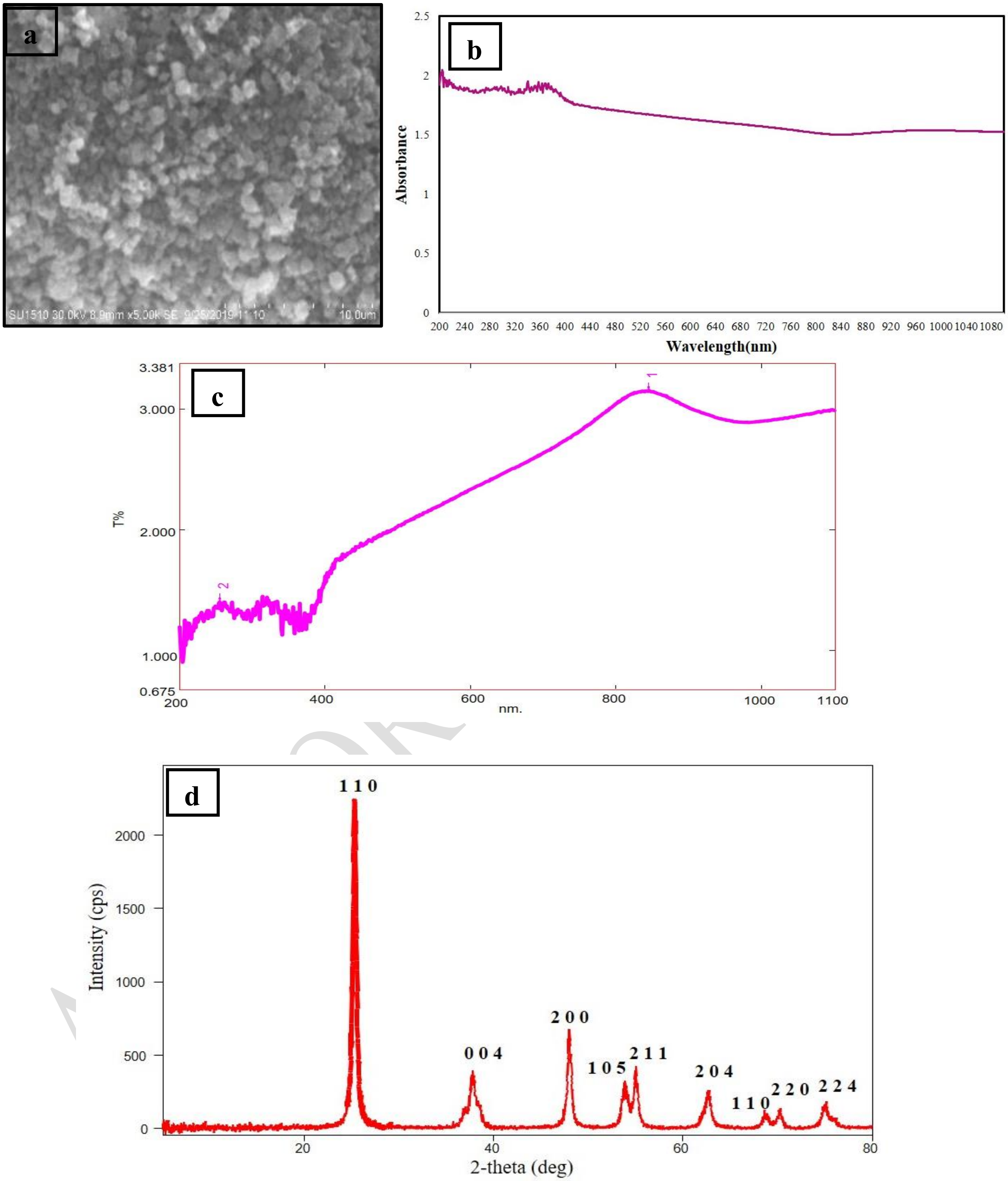

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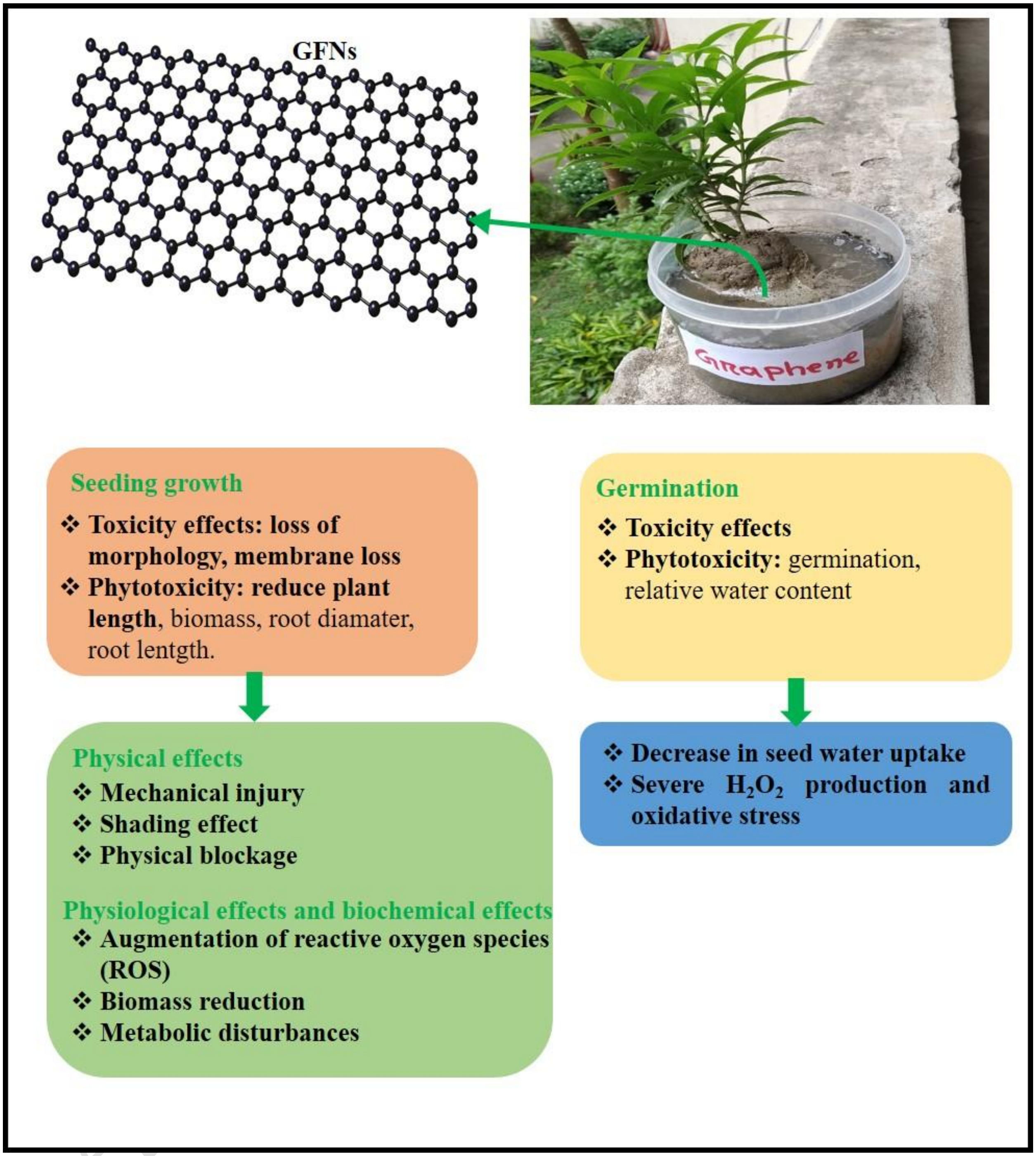

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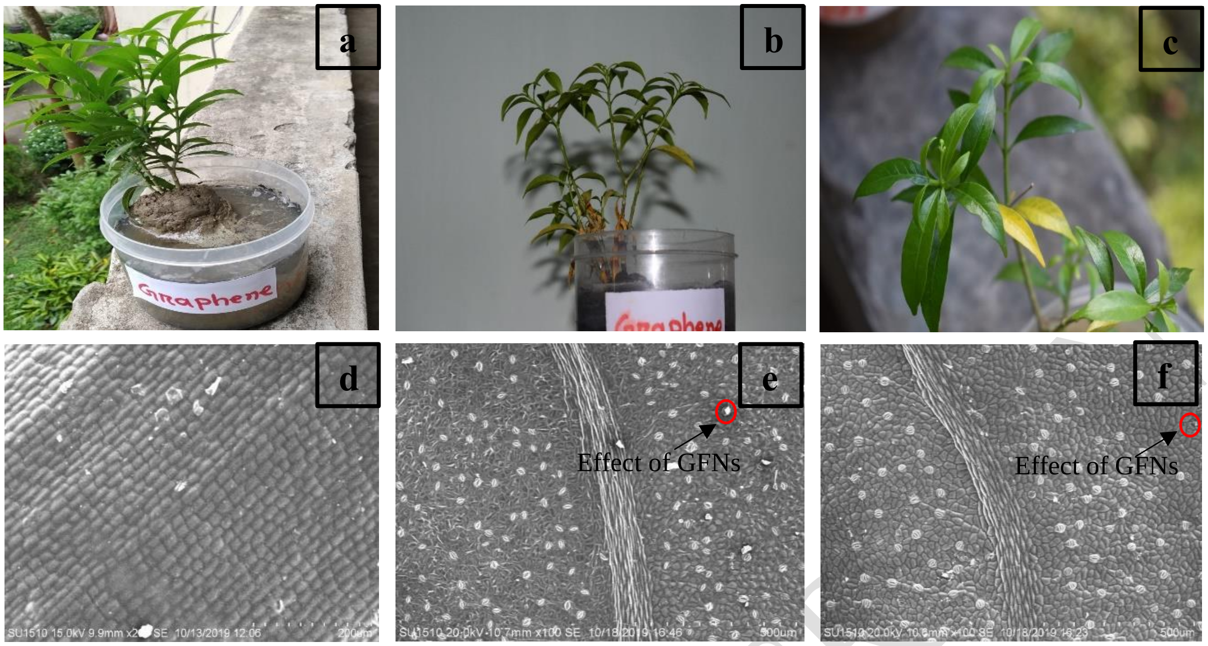

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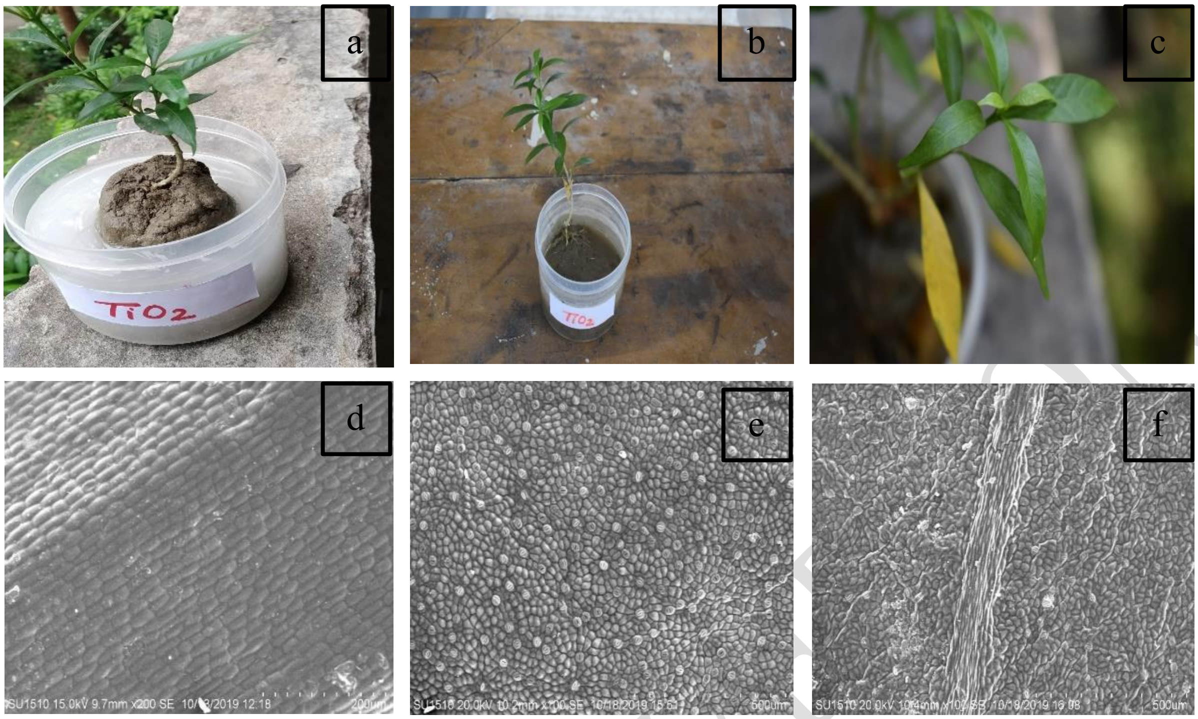

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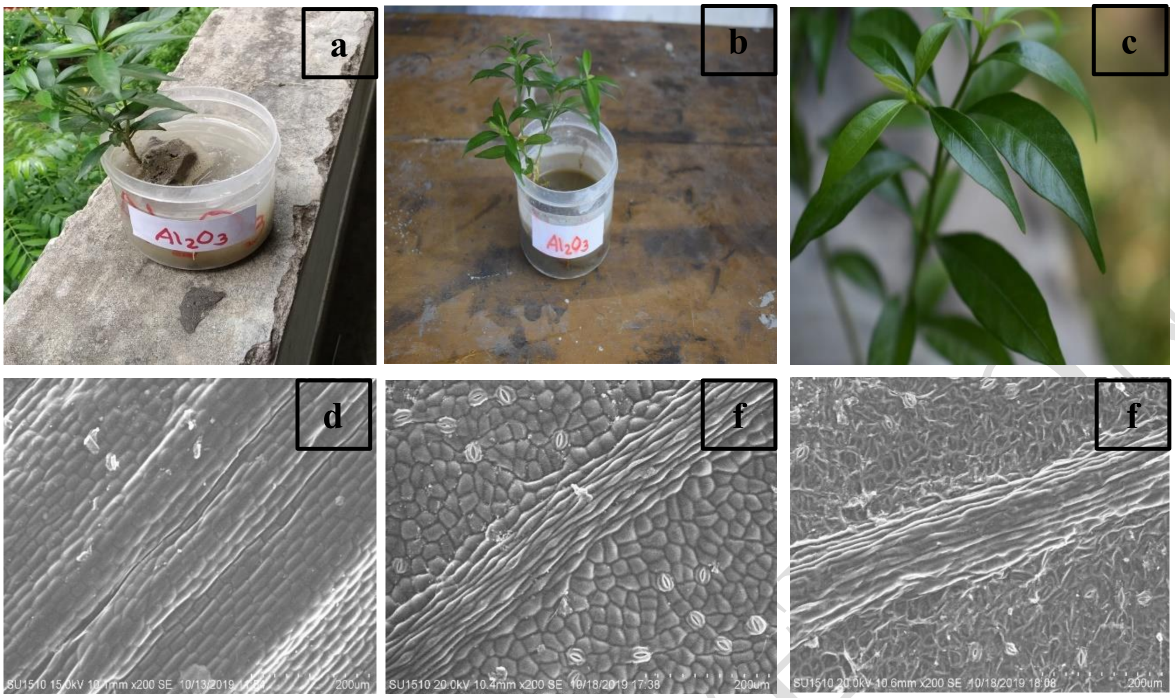

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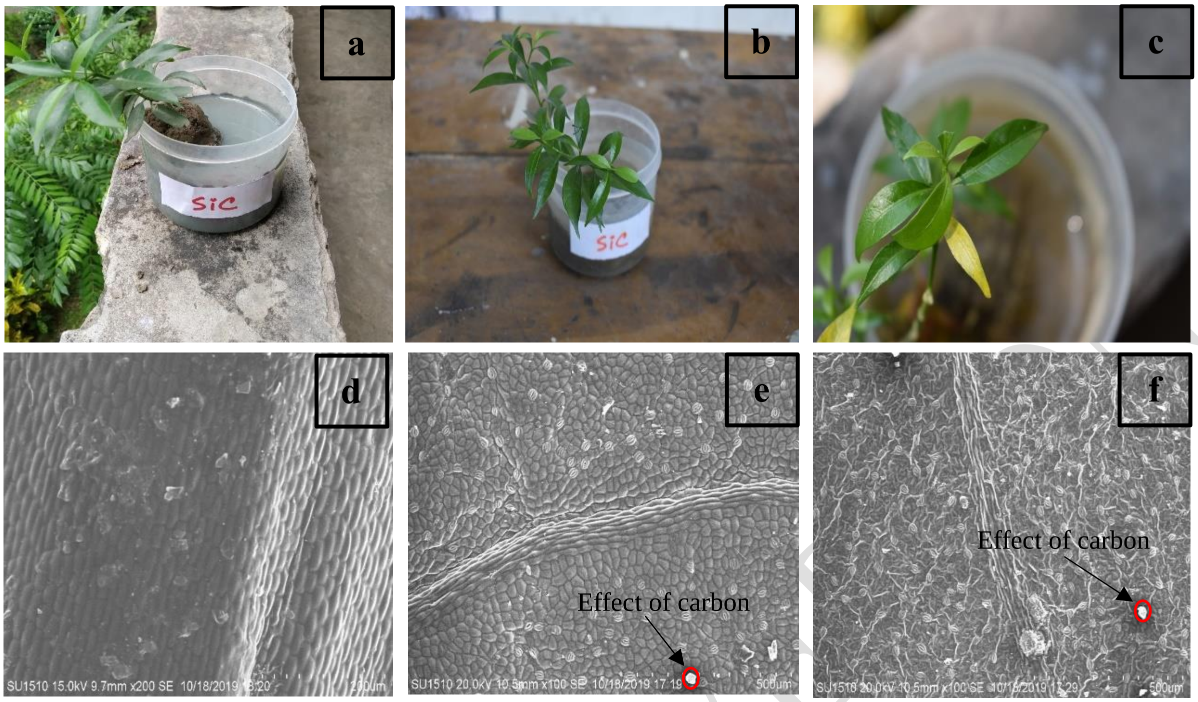

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