SYNTHESIS OF CeO_2/SiO_2 NANO MATERIALS AND APPLICATION FOR STIMULANTING GROWTH OF BELL PEEPPER PLAN (*Capsicum Annuum L.*)

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TÓM TẮT

TỔNG HỢP VẬT LIỆU NANO CeO_2/SiO_2 ỨNG DỤNG LÀM CHẤT KÍCH THÍCH SINH TRƯỞNG CHO CÂY ỚT CHUÔNG (*Capsicum Annuum L.*)

Trong nghiên cứu này, vật liệu CeO_2/SiO_2 được tổng hợp và ứng dụng làm chất kích thích sinh trưởng cây ớt chuông từ tiền chất $Ce(NO_3)_4$ và tro trấu bằng phương pháp chiếu xạ gamma. Hình thái và cấu trúc vật liệu được xác nhận thông qua các phương pháp đặc trưng hóa lý bao gồm: đặc trưng XRD, EDX, IR và SEM. Kết quả khảo sát ảnh hưởng của vật liệu CeO_2/SiO_2 đến sự sinh trưởng phát triển của cây ớt chuông cho thấy, CeO_2/SiO_2 ảnh hưởng đáng kể đến sự sinh trưởng, phát triển của cây ớt chuông. Dữ liệu thực nghiệm thu được chỉ ra rằng năng suất ớt chuông tăng 22 tấn/ha, chiều dài rễ trung bình tăng 3,6 cm và thời gian thu hoạch ít hơn 11 ngày so với mẫu đối chứng. Ngoài ra, cây ớt chuông có bổ sung CeO_2/SiO_2 thì cứng cáp hơn và không có hiện tượng vàng lá. Điều này cho thấy CeO_2/SiO_2 có tác dụng kích thích sinh trưởng đối với cây ớt chuông.

Từ khoá: *CeO_2, SiO_2, kích thích sinh trưởng thực vật, ớt chuông, năng suất.*

1. INTRODUCTION

In agriculture, silicon is not considered an essential element (out of the 16 essential elements for crops), but it plays an important role for crops [1-4]. Most soils are naturally rich in silicon, constituting 60-70% depending on the soil type [4]. However, the crucial point is that silicon exists in the soil in a form that is structurally difficult for crops to absorb and utilize. Soils can become deficient in silicon, especially in tropical conditions where silicon can be continuously leached away, and additionally, significant amounts of silicon are removed by crops each year. According to Miyake and Takahashi (1978), the improved resistance of plants to fungal invasion may also be attributed to the accumulation of Si in the epidermal cell layer [2-3]. Research across various crop types has shown that Si positively influences the plants' resilience by enhancing the Si content, thus protecting them from pest attacks [5-8]. Many studies suggest that plants uptake silicon in the form of SiO_3^{2-} passively through transpiration, with selective absorption facilitated by metabolic processes through the plant root system [9-13]. It is evident that Rare earth elements increase nutrient uptake and accumulation, enhance synthesis rates, and boost the accumulation and transport of sugars in cereals [14-16]. Their presence also elevates sugar levels in sugarcane, sugar beets, and watermelons, increases fructose and vitamin C content in fruits, and enhances the spiciness and aroma of pepper seeds. These roles contribute to increased crop yields when using fertilizers containing rare earth elements. Additionally, bell peppers, also known as sweet peppers, are rich in essential nutrients. Currently, bell peppers come in common colors such as red, yellow, green, and orange. Each color variation signifies distinct nutritional compositions, offering valuable health benefits to consumers [17]. Lutein and zeaxanthin present in bell peppers help improve eye health, guarding against the harmful effects of blue light and oxidative damage to the macular region of the eye. Furthermore, they aid in visual improvement and limit oxidative reactions damaging the retina. Moreover, bell peppers contain iron, a prominent mineral that enhances blood quality, preventing anemia risks. Additionally, they are rich in vitamin C, polyphenols, and flavonoids, which combat harmful free radicals, enhance blood circulation, and effectively protect cardiovascular health [17-19]. Recently, bell peppers have been introduced for cultivation in Lam Dong province, and preliminary results indicate their adaptability to soil conditions, particularly suitable for greenhouse cultivation.

The research and synthesis of CeO_2/SiO_2 nano-materials have been successfully conducted by numerous scientists, such as the research group led by J. Lin et al. [20], utilizing the hydrothermal method at 523 K for 3 hours to obtain a CeO_2/SiO_2 nano-mixture, which was applied for fluoride ion treatment in water. In 2018, the research team led by Nguyen Thi Ha Chi from the Materials Institute, Vietnam Academy of Science and Technology, successfully synthesized CeO_2 nano-materials on SiO_2 substrate from precursors $Ce(NO_3)_3$ and 30 nm nano SiO_2 through the gel combustion method, applied in environmental treatment [21]. Christy E J S, Alagar R., Dhanu M, and Pius A. (2020), successful synthesis of CeO_2/SiO_2 bulk materials have been applied in treating organic compounds with high efficiency [22]. Nguyen Viet Bac and colleagues (2021) successfully synthesized CeO_2/SiO_2 dispersed in polyurethane, applied in paint technology [23]. Despite numerous studies on synthesizing the mentioned material systems, there hasn't been any research published on using waste materials in Viet Nam and gamma irradiation methods. This is a novel research direction utilizing waste materials to synthesize nano-silica with a porous structure along with nano-ceria.

Therefore, in this study, CeO_2/SiO_2 materials were synthesized using the gamma irradiation method and applied as growth stimulants for bell pepper plants to contribute to increased productivity and nutritional quality.

2. EXPERIMENTAL

2.1. Materials, Chemicals, and Equipment

Materials: Bell pepper seedlings purchased from Dalat Hasfarm, rice husk ash obtained from Hoai An district, Binh Dinh province.

Chemicals: All chemicals and solvents met analytical standards: acetic acid (Sigma-Aldrich), $Ce(NO_3)_3.6H_2O$

(Merck), KOH (Sigma-Aldrich), HCl (Merck), chitosan (Merck), urea fertilizer (VN), potassium fertilizer (VN), phosphate fertilizer (VN).

2.2 Material Synthesis

2.2.1 Synthesis of SiO_2 Material from Rice Husk Ash

Weigh 50 grams of rice husk ash treated with 1 M HCl acid into a Teflon beaker, add 150 mL of 6.5 M KOH solution. Proceed to heat the mixture (maintaining constant volume) using a magnetic stirrer with a reflux system for 120 minutes at 90 °C. Then continue stirring until the mixture cools completely. Filter to collect the K_2SiO_3 solution. Disperse the K_2SiO_3 solution in 5% chitosan solution at a 1:1 volume ratio. Adjust the pH to 6 with 4 M CH_3COOH acid solution, yielding a mixture of silica and CH3COOK salt (mixture A). Mixture A is dissolved in 5 liters of distilled water and irradiated with a dose of 20 Kgray for 12 hours to obtain solution B.

2.2.2 Synthesis of CeO_2/SiO_2 Material

Dissolve 3.94 g of $Ce(NO_3)_3.6H_2O$ in 50 mL of distilled water. Slowly add the $Ce(NO_3)_3$ solution dropwise into 75 mL of 5% chitosan solution contained in a glass beaker and stir continuously for 2 hours to obtain solution C. Gradually add solution C into solution B (with a CeO_2/SiO_2 volume ratio of 1/1) to obtain solution D. Subject solution D to gamma irradiation with a dose of 20 Kgray for 12 hours to obtain the CeO_2/SiO_2 nano-material system.

2.3 Material Characterization

The phase composition is determined using X-ray diffraction (D8-Advance 5005). Chemical bonding characteristics of the synthesized materials are determined using infrared spectroscopy (IR-Tensor-27, Bruker). The presence of elements in the synthesized material samples is analyzed using energy-dispersive X-ray spectroscopy (Jeol 5410 equipment). Surface morphology is examined using scanning electron microscopy (JEOL JSM-6500F).

2.4 Experimental Investigation of the Effects of CeO_2/SiO_2 on Bell Pepper Growth

A 300 m^2 planting area is divided into 6 experimental plots, with 3 control plots and 3 experimental plots supplemented with CeO_2/SiO_2 (1000 ppm) to stimulate plant growth. The CeO_2/SiO_2 material is mixed in appropriate ratios for each growth stimulation period and sprayed onto the leaves. During the stage of the plant having 5-7 true leaves, spray once a month. When bell pepper plants begin to flower, spray twice a month.

The control plots are planted following the bell pepper cultivation technique outlined by the Agricultural Institute [24] as follows: Planting is done on November 5, 2023, with a spacing of 30 x 20 cm; fertilizer application per hectare includes 20 tons of compost, 200 kg of urea, 500 kg of superphosphate, and 300 kg of potassium fertilizer (K_2O).

For the experimental plots supplemented with CeO_2/SiO_2: 1 liter of Stripping process.

3. RESULTS AND DISCUSSION

3.1 Material Characteristics

To determine the compositions of CeO_2, SiO_2, and CeO_2/SiO_2 materials, the synthesized materials were characterized using the X-ray diffraction (XRD) method, and the results are presented in Figure 1. On the X-ray diffraction pattern of SiO_2, a broad diffraction peak with a large full width at half maximum (FWHM) appears at around 23° 2-theta [21, 23]. Meanwhile, the XRD pattern of

CeO_2 exhibits strong diffraction peaks observed at 27, 28, 39, and 48° 2-theta corresponding to the (220), (300), (400), and (622) planes, respectively (according to JCPDS standard 04 - 0856) [23]. In contrast, the X-ray diffraction pattern of CeO_2/SiO_2 materials shows sharp characteristics.

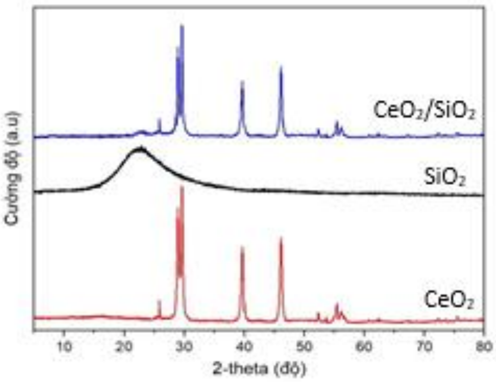

Figure 1. XRD patterns of $CeO_{2,}$, SiO_2, and CeO_2/SiO_2 materials

To determine the elemental composition present in the CeO_2/SiO_2 materials, the materials were characterized using energy-dispersive X-ray spectroscopy (EDX). The results are presented in Figure 2. The energy-dispersive X-ray spectra of CeO_2, SiO_2, and CeO_2/SiO_2 materials in Figure 2 indicate that characteristic peaks with strong intensities for Si, O, and Ce appear at energy levels of 1.88, 0.50, and 4.62 KeV, respectively. The EDX spectra show the presence of characteristic peaks for both SiO_2 and CeO_2 components in the CeO_2/SiO_2 materials, with no presence of foreign elements [23].

The bonding characteristics in CeO_2, SiO_2, and CeO_2/SiO_2 materials reveal spectral bands at 649 cm^{-1} corresponding to the stretching vibrations of Ce-O bonds in CeO_2 [21] and a sharp and intense band at 3625 cm^{-1} attributed to the stretching and bending vibrations of O-H in the Ce-O-H group [21]. In contrast, the infrared spectrum of SiO_2 exhibits an intense absorption band at 1115 cm^{-1} characteristic of the stretching vibrations of O-Si-O (siloxane), at 1594.73 cm^{-1} corresponding to the bending vibration of the -OH group, vibrations around 800 cm^{-1} may be attributed to the vibrations of Si-OH groups (silanol) and vibrations at around 475 cm^{-1} are attributed to Si-O stretching [22-23]. The spectral bands at 3421 cm^{-1} and 1625 - 1490 cm^{-1} could be assigned to the O-H vibrations of water absorbed on the material surface [23]. Meanwhile, in the infrared spectrum of CeO_2/SiO_2 material, characteristic peaks for both SiO_2 and CeO_2 components are fully observed.

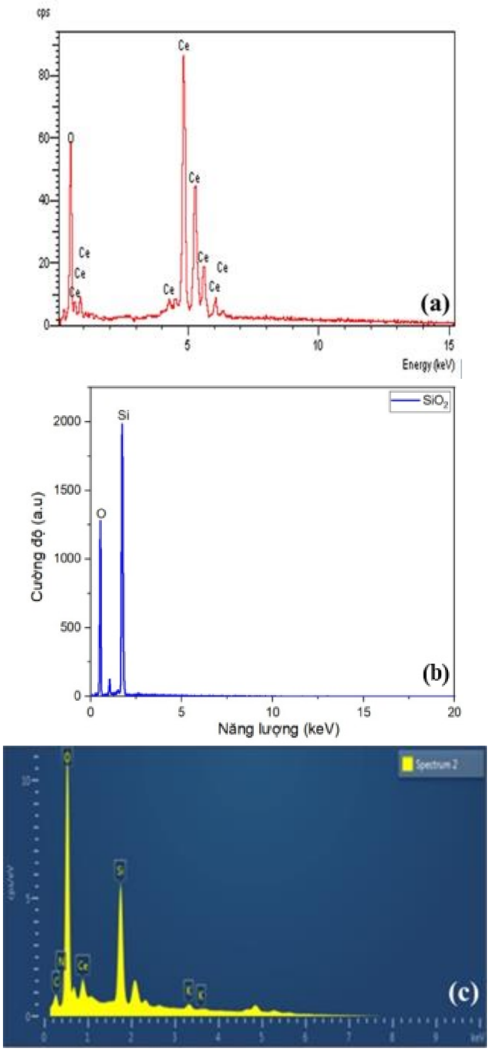

Figure 2. EDX spectra of CeO_2 (a), SiO_2 (b), and CeO_2/SiO_2 (c) materials

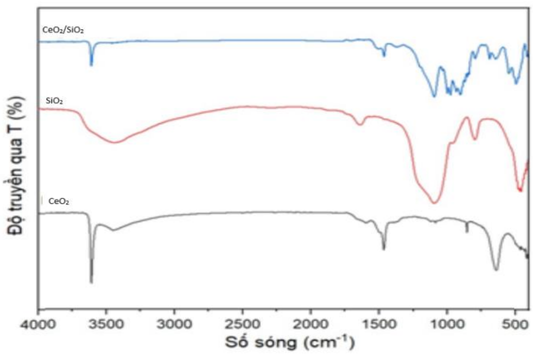

Figure 3. Infrared spectra of CeO_2, SiO_2 and CeO_2/SiO_2 materials.

SEM images of Figure 4 showing that the CeO_2 material consists of particles with diverse shapes, with an average size of about 40 - 50 nm, but tends to agglomerate. Meanwhile, the SiO_2 material also consists of aggregated particles, creating a rough, uneven surface with sizes ranging from 50 - 100 nm. As for the CeO_2/SiO_2 material, there is a dispersion of CeO_2 particles on SiO_2, resulting in a rough, uneven surface with sizes ranging from 50 - 80 nm.

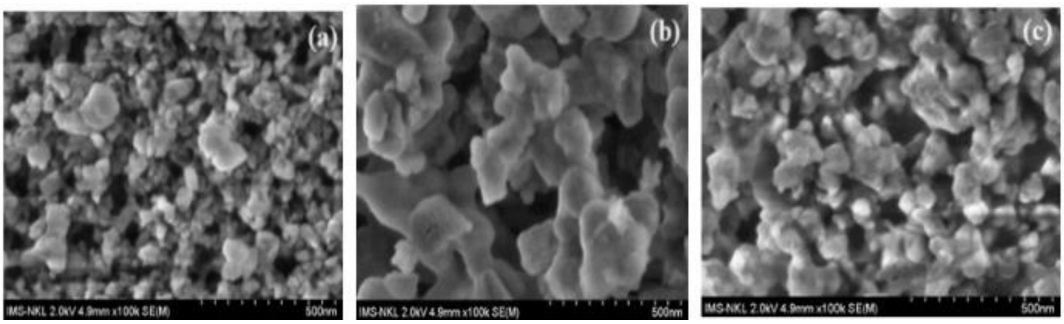

Figure 4. SEM images of CeO_2 (a), SiO_2 (b), and CeO_2/SiO_2 (c) materials

3.2 Impact of CeO_2/SiO_2 on the Growth of Bell Pepper Plants

Table 1. Parameters related to the growth and development of bell pepper plants when using CeO_2/SiO_2 materials

Parameter	Control (n=50)	CeO_2/SiO_2 (n=50)
Planting time	05/10/2023	05/10/2023
Harvest time	(8/1/2024)	(30/12/2023)
Average main root length (cm)	25,6 ± 0,3	31,2 ± 0,5
The achieved performance compared to the theoretical (%)	97,9 ± 0,2	138,6 ± 0,2
Leaf color	Green with yellow and wilted leaves	Dark blue

(Use Minitab 18 statistical software)

The results of the investigation into the effect of CeO_2/SiO_2 on the growth and development of bell pepper plants are presented in Table 1. The phenomenon of leaf yellowing in bell pepper plants without the addition of CeO_2/SiO_2 material (control group) is shown in Figure 5.

Figure 5. Bell pepper plant without (control)and with the addition of CeO_2/SiO_2 material (b)

Experimental results from growing bell pepper plants with the addition of CeO_2/SiO_2 material show that in the control group, the fruit yield reached 57 tons/ha, with the main roots averaging 25.6 cm in length, and the growth period until harvest was 94 days. Meanwhile, in the group supplemented with CeO_2/SiO_2 material, the fruit yield reached 79 tons/ha (an increase of 38.60% compared to the control group), with the main roots averaging 31.2 cm in length and the growth period until harvest was 86 days. Additionally, the main roots exhibited uniform size, deep green leaves, and no symptoms of leaf yellowing compared to the control group. This can be explained by the influence of Si on lignin synthesis; a deficiency in Si significantly reduces lignin content. Si acts as a nutrient that enhances plant growth, rigidity, improves crop yield, and produce quality. Furthermore, silica and ceria compounds stimulate the growth and development of plant roots, promote photosynthesis, enhance absorption of both macro and micronutrients and exhibit good resilience in adverse weather conditions. Therefore, the addition of CeO_2/SiO_2 to bell pepper plants has made them sturdier, with stronger root development, resulting in increased bell pepper yield.

4. CONCLUSION

Successful synthesis of CeO_2/SiO_2 material using the gamma irradiation method has been achieved. Investigation into the impact of CeO_2/SiO_2 material on the growth of bell pepper plants indicates that growth, development, and yield increase with the addition of CeO_2/SiO_2 nano fertilizers compared to the control sample.

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