MINISTRY OF EDUCATION AND TRAINING

VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY

GRADUATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

**Nguyễn Thị Thanh Huyền**

# FABRICATION AND RESEARCH ON THE CHARACTERISTICS OF NANO $Fe^0$, $Cu^0$, $Co^0$ DIRECTIONS FOR APPLICATION IN AGRICULTURE

**SUMMARY OF DISSERTATION ON SCIENCES OF MATTER**

**Major: Inorganic chemistry**

**Code: 9.44.01.13**

**Hà Nội - 2024**

This thesis was completed at: Graduate university of Science and Technology, Vietnam Academy of Science and Technology

Người hướng dẫn khoa học : Assoc. Prof.  Hoang Anh Son

Cơ quan công tác: Institute of Materials Science, Vietnam Academy of Science and Technology.

Reviewer 1: ………………………

Reviewer 2: ……………………….

Reviewer 3: : ……………………….

This thesis will be defended at Graduate University of Science and Technology, Vietnam Academy of Science and Technology at hour date month 2024.

The thesis can be found in:

- The Library of Graduate University of Science and Technology, Vietnam Academy of Science and Technology.
- National Library of Vietnam.

## LIST OF PUBLICATIONS RELATED TO THE DISSERTATION

1. Nguyen Thi Thanh Huyen, Nguyen Hong Nhung, Le Thanh, Pham Duy Khanh, Tran Dai Lam and Hoang Anh Son, 2018, *Preparation and characterization of zerovalent iron nanoparticles*, Vietnam Journal of Chemistry, 56(2), 226-230.
2. Huyen Nguyen Thi Thanh, Son Hoang Anh, Nhung Hong Nguyen, Chi Que Tran, Dong Nguyen Van, Quy Vu Ngoc, 2018, *Research on the impact of nano metals particle in growth development and yield of maize*/ The 9$^{th}$ International Workshop on Advanced Materials Science and Nanotechnology (IWAMSN2018), 8-12 November, Ninh Binh City, Vietnam.
3. Nguyễn Thị Thanh Huyền, Nguyễn Hồng Nhung, Phạm Duy Khánh, Trần Quế Chi, Trần Thị Thanh Thảo, Hoàng Anh Sơn, 2019, *Chế tạo và nghiên cứu đặc trưng tính chất của hạt nano coban hóa trị không*. Tạp chí Hóa học, 57(4e1,2) 264-268.
4. Son Hoang Anh, Nhung Nguyen Hong, Chi Tran Que, Yen Hoang Quach Thi, Toan Nguyen Thi, Huong Tran Thi, Chan Do The, Sơn Le Phuc, Trung Nguyen Quoc, Son Vu Hong, Huyen Nguyen Thi Thanh and Chi Phan, 2016, *Preparation and study physicochemical characterization of zero – valent iron, copper and cobalt nanoparticles*. Proceedings The 8th International Workshop on Advanced Materials Science and Nanotechnology, 405-415.
5. Son A. Hoang, Hanh H. Cong, Shukanov V. P., Karytsko L. A., Poljanskaja S. N., Melnikava E. V., Mashkin I. A., Huyen T. Nguyen, Khanh D. Pham and Chi M. Phan, 2022, *Evaluation of metal nano-particles as growth promoters and fungi inhibitors for cereal crops*/ Chem. Biol. Technol. Agric. 9:12 https://doi.org/10.1186/s40538-021-00277-w
6. Hoàng Anh Sơn, Công Hồng Hạnh, Nguyễn Thị Thanh Huyền, Phạm Duy Khánh. Bằng độc quyền sáng chế số 31198 của Cục sở hữu trí tuệ thuộc Bộ Khoa học và Công nghệ, 2022, *Phương pháp xử lý củ gừng giống( zingiber officinale) bằng dung dịch nano kim loại coban hóa trị không ($Co^0$) để tăng năng suất thu hoạch.* 2022.
7. Hoàng Anh Sơn, Trần Quế Chi, Nguyễn Quốc Trung, Quách Thị Hoàng Yến, Nguyễn Thị Thanh Huyền, Đàm Văn Phú, Lê Trọng Hính, Vũ Ngọc Quý, 2017, *Ứng dụng hạt nano kim loại để xử lý hạt giống nhằm kích thích sinh trưởng và tăng năng suất thu hoạch của cây ngô*. Tạp chí Hóa học 55(3e12), 204-209, ISSN: 0866-7144

# I. THESIS INTRODUCTION

## 1. Urgency of the topic

The agricultural sector is currently facing a series of global challenges such as: the world's population is growing rapidly, the area of arable land is increasingly shrinking, climate change issues, or environmental issues such as pesticide residues, fertilizers...

Therefore, the need to change traditional farming methods with new agricultural techniques to save costs, improve productivity, crop quality, and ensure environmental safety is very necessary. The application of nanotechnology in the agricultural sector promises to solve these problems.

Indeed, nanotechnology applied to agriculture is currently being researched mainly in five aspects. One is stimulating plant growth. Two is increasing crop yield. Three is protecting plants. Four is improving soil quality. Five is intelligent monitoring of pathogens and pesticide residues.

Along with the recent vibrant development of nanotechnology, scientists have studied the effects of nano-sized trace elements (<100 nm) on plants. The effects of nanoparticles can be through stages such as seed treatment before planting, combined in foliar fertilizers, slow-release fertilizers, herbicides, pesticides, etc.

When treating seeds with nano metals, typically nano copper, iron, cobalt... they have the effect of destroying microorganisms, protecting seeds from pathogens. In addition, they also create unfavorable conditions for pathogenic microorganisms in the soil, and at the same time they are absorbed by plants as trace elements that stimulate plant growth. Trace elements increase moisture through the seed coat, activate biochemical processes in the seed, increase the viability, germination, and growth of above-ground parts as well as the root system. The stronger the germination ability of seeds, the less the consumption of reserve nutrients, the more the plant's respiration, allowing seeds to germinate and sprout even with a small amount of nutrients in the endosperm. In fact, farmers have often used metals in the form of salts or chelate complexes to treat seeds, spray, and fertilize. However, the toxicity of metals in nano-particle form is proven to be 10-40 times smaller than the toxicity of the salts of those metals. Using nano-metals to treat seeds before planting to replace current conventional seed treatments, contributing to improving crop yields and minimizing environmental pollution is an extremely necessary measure to develop a clean, safe and environmentally friendly agriculture.

Among the trace elements, copper has a particularly important meaning in the life of plants and cannot be replaced by any other element. Copper is the main component of enzymes concentrated in plant roots, participating in the nitrogen metabolism and oxidation process occurring in plant cells and it is in the basic components of oxidizing enzymes. Under the effect of copper, plant respiration increases dramatically, increasing the chlorophyll content and its resistance. Next is iron, iron is an important catalyst in the production of chlorophyll, which gives leaves their green color. Iron affects many synthesis and metabolism processes of organic compounds, including cytochromes - a transmitting agent, participating in the respiratory process and even entering the composition of peroxide oxidizing enzymes and catalysts. In addition, it is a component of the iron complex, a functional compound among the transfer agents (transporters) in the process of photosynthesis, reduction of $NO_3^-$ and $SO_4^{2-}$ , nitrogen assimilation and chlorophyll biosynthesis. Cobalt belongs to the group of super-trace elements, is a catalyst for many biochemical reactions of plants, related to the process of nitrate reduction and nitrogen synthesis. Cobalt is a central component of vitamin cobalamin, or vitamine B-12. Cobalt has a positive effect on the accumulation of chlorophyll, increases the strength of the bond of chlorophyll complexes with proteins and their resistance to destruction in the dark. Thus, among the trace elements necessary for plants, iron, copper and cobalt are the three indispensable and most important elements.

On the other hand, among food crops in our country, corn is currently the main crop after rice, and among medicinal plants, ginger is currently a crop that plays a role in hunger eradication and poverty reduction, bringing high economic efficiency in many localities, especially in the northern mountainous provinces. However, corn and ginger production currently mainly uses traditional farming methods, depending entirely on natural conditions, leading to low crop yields. Therefore, applying science and technology, choosing smart farming models combined with using nano-metal preparations to treat seeds is the core solution to increase crop yields. In addition, the study not only studies the effects of metal nanoparticles on the growth and development of plants in tropical climates, but also studies the effects of metal nanoparticles on the growth and development of wheat and barley plants grown in temperate climates.

Therefore, the choice of research direction to manufacture zero-valent nanoparticles of three metals $Fe^0$, $Cu^0$, $Co^0$ to survey and evaluate their impact on the growth and development, increasing productivity of some specific crops such as corn, ginger in tropical climate conditions and wheat, barley in temperate climate conditions in the doctoral thesis has both novelty and scientific significance and practical value in the country and in the world.

Based on the above scientific and practical requirements, the doctoral student chose the topic "Manufacture and study of properties of nano metals $Fe^0$, $Cu^0$, $Co^0$ oriented to application in agriculture" as his doctoral thesis.

**2. Research objectives of the thesis:**

- Fabrication of nanocrystals of metals Fe, Cu, Co with zero valence ($Fe^0$, $Cu^0$, $Co^0$) with size under 100 nm by reduction method with newly generated hydrogen.
- Find suitable conditions for pre-treatment of corn, wheat, barley/ginger seeds with zero-valent metal nanoparticles ($Fe^0$, $Cu^0$, $Co^0$).

- Evaluate the ability to stimulate growth during the germination stage, stem, root, leaf development, the ability to increase yield of corn, ginger, wheat, barley after seed treatment with nano $Fe^0$, $Cu^0$, $Co^0$ and their mechanism of action.

**Thesis research content :**

1. Research on the fabrication and characterization of metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$
2. Research on the preparation and physicochemical characteristics of seed treatment solution based on metal nano suspension solution.
3. Investigate the effects of metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$ on growth, development, yield, and product quality of corn, ginger, wheat, and barley.

**4. Thesis layout**

The thesis with 116 pages includes 3 chapters. Chapter 1: Overview. Chapter 2: Experiments and research methods. Chapter 3: Results and discussion.

## II. THESIS CONTENT

## CHAPTER 1. RESEARCH OVERVIEW

Study and collect scientific information related to metal nanomaterials, including characteristic properties and methods of manufacturing metal nanomaterials. On that basis, propose methods of manufacturing metal nanomaterials as well as chemicals suitable for the topic. The method of manufacturing 3 metal nanomaterials Fe, Cu, Co is chosen as the chemical reduction method with hydrogen gas as the reducing agent. Hydrogen gas produced from the water electrolysis reaction is used directly to enhance the efficiency of the reduction process.

Studying some viewpoints on the mechanism of action of super-dispersed metal nanoparticles on plants shows that the mechanism of action of nanoparticles is very complicated because they act simultaneously on many objects and many processes occurring inside the cell, at the center of the cell or the entire system, in which the active center of enzymes can be the object of action of nanoparticles. There are many studies by scientists around the world that have proven the effectiveness of the application of metal nanoparticles on plants. However, up to now, there has been no clear study on the mechanism of action of super-dispersed metal nanoparticles on plants and there is still much controversy. In this thesis, I assume that the object of action of nanoparticles is the active center of enzymes.

An overview of the domestic and foreign research on the application of metal nanoparticles in the field of cultivation shows that metal nanoparticles have the effect of promoting plant growth and are of great interest in the field of application in agricultural production. There have been many studies by scientists in the world as well as in the country that have proven the effects of metal nanoparticles on plants. However, there is still a lack of in-depth research on a form of zero-valent metal nanoparticles, methods and conditions for their synthesis, their characteristic physical-chemical-biological properties in the metallic state as well as when converted into energy-rich solutions for seed treatment before planting.

Therefore, the choice of research direction to manufacture zero-valent Fe, Cu, Co metals nano by hydrogen reduction method and to investigate their physical-chemical properties, their effects on growth, development and productivity of some crops through the process of seed/tubers treatment before planting in the thesis has novelty and scientific significance as well as practical value both domestically and internationally.

# CHAPTER 2: EXPERIMENT AND RESEARCH METHODS

## 2.1. Chemicals, materials and equipment

### *2.1.1. Chemicals*

Chemicals used in the study High purity, produced by Merck of Germany, including: Iron nitrate $Fe(NO_3)_3.9H_2O$, copper sunfat $CuSO_4$

$.5H_2O$, cobalt nitrate $Co(NO_3)_2.6H_2O$, sodium hydroxide NaOH, ammonium hydroxide $NH_4OH$.

### *2.1.2. Materials*

The corn seeds are hybrid corn LVN-10, a single hybrid of the Maize Research Institute. The ginger roots are the traditional buffalo ginger variety commonly grown in Ha Quang district, Cao Bang. The wheat and barley seeds are early-ripening varieties of Belarus, commercially produced by Evro- Semena, Belarus.

### *2.1.3. Equipment*

Hydrogen electrolyzer (USA, model HGH -300). Nabertherm temperature controlled tube furnace (Germany model R 50/500/12) . Elmasonic S60H ultrasonic vibrator. pH meter 7110. High speed refrigerated centrifuge. Frichs planetary ball mill ( Germany ).

## 2.2. Fabrication of metal nanomaterials $Fe^0$, $Cu^0$, $Co^0$

### *2.2.1. Preparation of precursors*

Process of making precursors: Add the corresponding metal salt ($Fe(NO_3)_3.9H_2O$, $CuSO_4.5H_2O$, $Co(NO_3)_2.6H_2O$) into distilled water, then stir until dissolved, we get a metal salt solution. Slowly drop NaOH solution or $NH_4OH$ solution into the metal salt solution to create a precipitate. The resulting precipitate is decanted, washed with distilled water many times to wash away all the ions. Centrifuge the resulting product, then dry it, heat it in air, then grind it finely to get the final product, oxide powder.

### *2.2.2. Fabrication of metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$*

Put the precursor into the ceramic boat and then put it into the reaction chamber. Then put the reaction chamber into the furnace. Install the gas pipe and safety valve. Electrolyze to create a flow of $H_2$ gas at a rate of 300ml/min. Heat slowly to the appropriate temperature. Let the furnace cool naturally while continuing to electrolyze to create a flow of $H_2$ gas to protect the sample. After the furnace cools, take the product out and store it in a vacuum environment.

### 2.2.3. Methods for studying the properties of materials and evaluating the impact of metal nanoparticles on plants

*2.2.3.1. Methods of studying the properties of materials*

The thesis used methods to study the characteristics of materials including: X - ray diffraction (XRD) to analyze the structure of the material. X-ray fluorescence (XRF) and energy dispersive spectroscopy (EDX) to analyze the chemical composition of the sample. Scanning electron microscopy (SEM) to evaluate the morphology and size of the particles . Zeta spectrum method, DLS dynamic light scattering method: determine the distribution of particle size and Zeta potential . BET method : Determine the specific surface area of the sample .

*2.2.3.2. Methods for assessing the impact of metal nanoparticles on plants*

*a. Method of treating seeds/tubers with nano-lim particles*

The metal nano suspension solution is made by dissolving a certain amount of metal nano into a volume of distilled water (deionized) at a predetermined concentration, used to treat seeds. Put the mixed solution into an ultrasonic vibrator and turn it on continuously for 10 to 40 minutes. Under the influence of ultrasonic waves, the metal nano particles participate in the reduction reaction and are transformed into a suspension in the water environment.

Seeds/tubers are soaked in a suspension of metal nanoparticles for a specific period of time, then removed and planted immediately for best results. Based on the quantity of seeds/tubers sown per hectare, the mass of seeds/tubers and the amount of metal nanoparticles needed for treatment according to each experimental formula are calculated.

*b. Method for assessing the impact of metal nanoparticles on plants*

Methods for assessing the growth and development of corn and ginger plants according to national standards for testing the cultivation and use value of corn and ginger varieties. For wheat and barley, the determination is made according to current standards of the Republic of Belarus.

# CHAPTER 3: RESULTS AND DISCUSSION

## 3.1. Research results on the fabrication and characterization of metal nanomaterials $Fe^0$, $Cu^0$, $Co^0$

### *3.1.1. Results of manufacturing precursors $Fe_2O_3$, CuO, $Co_3O_4$*

The precursors $Fe_2O_3$, CuO, $Co_3O_4$ were prepared in powder form as precursors for the reduction reactions of $Fe^0$, $Cu^0$, $Co^0$ with relatively uniform shapes. The average particle size of $Fe_2O_3$ was 88.51nm, CuO had an average particle size of 81.17nm and purity was 99.96%, $Co_3O_4$ had an average particle size of 90.91nm. The properties of the precursors were determined by X -ray diffraction (XRD) , scanning electron microscopy (SEM), dynamic light scattering (DLS) and XRF methods.

### *3.1.2. Results of fabrication of $Fe^0$ metal nano*

To prepare nano $Fe^{0,}$ we investigated the effects of temperature and reaction time on the structure and particle size of the material, thereby finding the optimal temperature and time for calcining the sample. After investigating the selected sample calcination conditions, the temperature was 400°C and the time was 90 minutes. The properties of nano $Fe^0$ were determined by the following methods: XRD, SEM, XRF, BET, and DLS.

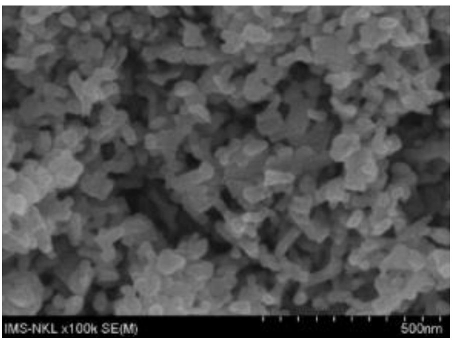



***Figure 3.1*** . SEM image of $Fe^0$ nano sample

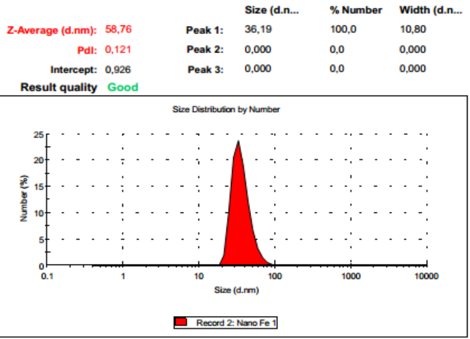



***Figure 3.2.*** Particle size distribution of $Fe^0$ nano sample

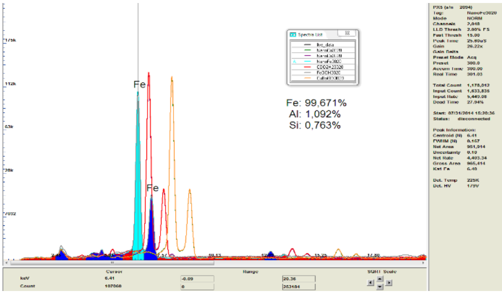



***Figure 3.3.*** Elemental composition analysis of $Fe^0$ nano sample

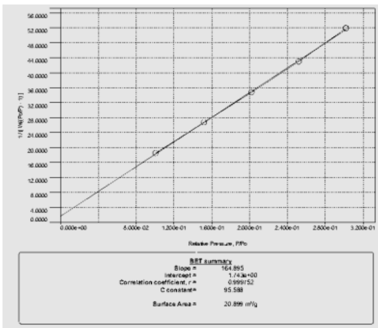



***Figure 3.4.*** BET specific surface area measurement of $Fe^0$ nano sample

By the reduction method by newly generated hydrogen from the electrolysis reaction of water with a flow rate of 300ml/min, we successfully prepared $Fe^0$ iron metal nano powder. from iron (III) oxide $Fe_2O_3$ at a reaction temperature of 400°C and a reaction time of 90 minutes. The obtained $Fe^0$ nanoparticles had an average size of 58.76nm and a purity of 99.67%.

### *3.1.3. Results of fabrication of $Cu^0$ metal nano*

The influence of reaction time and temperature on the structure and particle size of the material was investigated, thereby determining the optimal time for sintering the sample at 400°C and the duration at 60 minutes. The properties of $Cu^0$ nanoparticles were determined by the following methods: XRD, SEM, XRF, BET, and DLS.

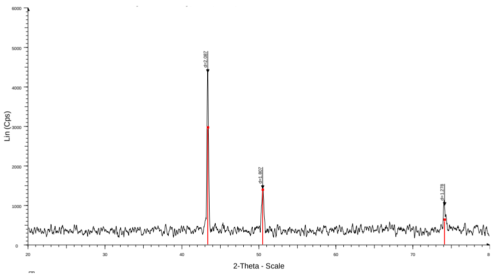



***Figure 3.5.*** XRD pattern of $Cu^0$ nano sample annealed at 400° C, 60 minutes

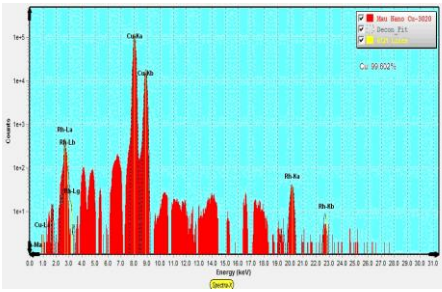



***Figure 3.6*** . Analysis of nano $Cu^0$ chemical composition by XRF method

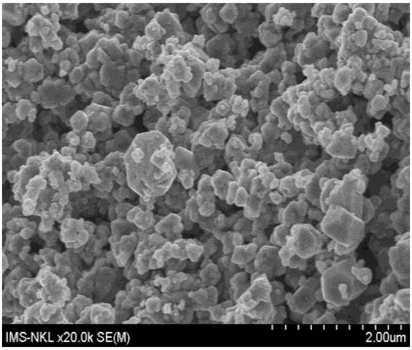



***Figure 3.7.*** SEM image of $Cu^0$ nano sample fabricated at 400°C/60 minutes

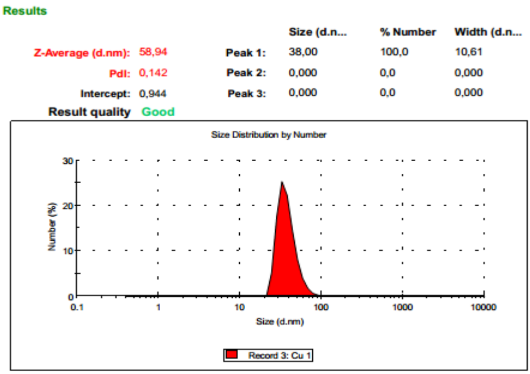



***Figure 3.8*** . Results of measuring the average grain size of the $Cu^0$ nano metal

By the reduction method by hydrogen generated from the electrolysis reaction of water. Successfully fabricated $Cu^0$ nano metal powder from copper (II) oxide CuO at a reaction temperature of 400°C, a reaction time of 60 minutes and a hydrogen gas flow of 300ml/min. The fabricated $Cu^0$ nano has an average size of 58.94nm, and a purity of 99.6%.

***3.1. 4. Results of fabrication of $Co^0$ nano metal***

The influence of temperature and reaction time on the structure and size of $Co^0$ nanoparticles was investigated , and the optimal temperature and time for calcination of the sample were determined at 500 °C and 60 minutes.

The properties of $Co^0$ nanoparticles were determined by the following methods: XRD, SEM, XRF, BET, and DLS.

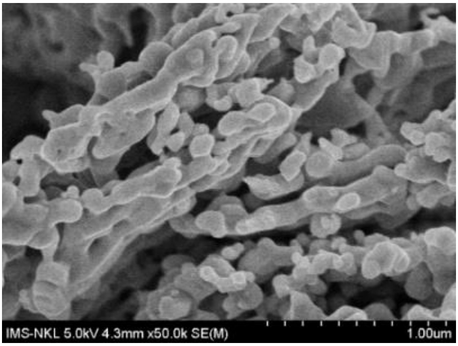



***Figure 3.9 .*** . Photo SEM of $Co^0$ at 500 $^oC$, reaction time 60 minutes

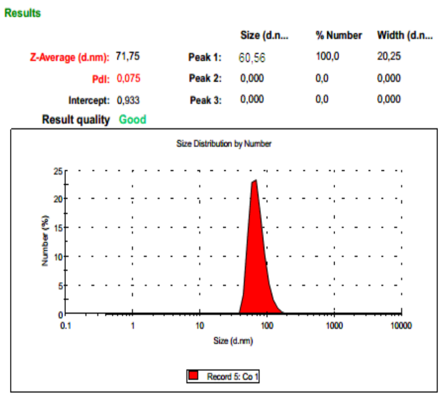
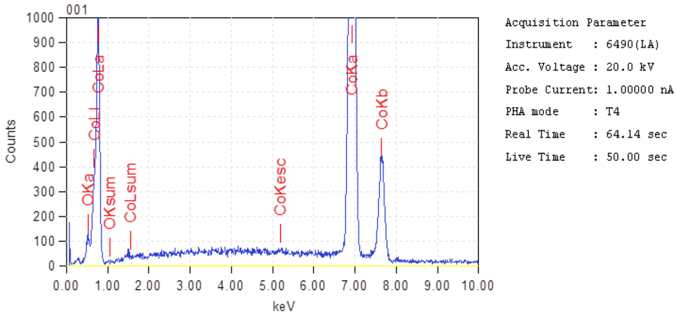



***Figure3.10.*** Particle size distribution of $Co^0$ nano samples prepared at 500$^oC$, reaction time 60 minutes




ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.1913

| Element | (keV) | Mass% | Error% | Atom% | Compound | Mass% | Cation | K |
|---|---|---|---|---|---|---|---|---|
| O K | 0.525 | 0.86 | 0.09 | 3.09 | | | | 1.0852 |
| Co K | 6.924 | 99.14 | 0.28 | 96.91 | | | | 98.9148 |

***Figure 3.11 .*** *EDX spectrum of* $Co^0$ nano sample fabricated at 500 °C, reaction time 60 minutes

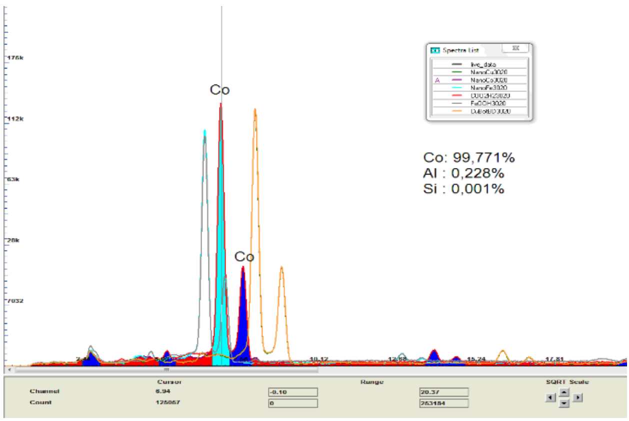



***Figure 3.12*** . Elemental composition analysis of $Co^0$ nano sample after reduction reaction by XRF method

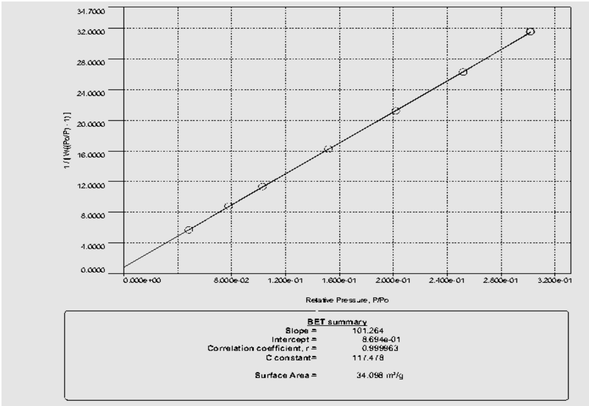



***Figure 3.13 .*** **BET** specific surface area measurement results of nano $Co^0$

Based on the analysis of XRD, EDX, XRF, BET and SEM results, the optimal conditions for preparing $Co^0$ nanomaterials are at a temperature of 500 $^oC$, a calcination time of 60 minutes, and a hydrogen gas flow rate of 30 ml/min. The obtained $Co^0$ nanomaterials are in the form of black, porous powder with an average size of 71.75 nm, and a purity of 98.91 to 99.71% (according to EDX and XRF).

**3.2. Research results on the preparation and characterization of suspension solutions of metal nanoparticles**

Making a suspension solution is an important step in the treatment of seeds before planting with metal nanoparticles. Metal nanoparticles in the process of creating a suspension solution by ultrasound will create highly active agents in the suspension solution, which can directly participate in reactions inside the cell, or act as catalysts for those reactions. Therefore, making a stable metal nano suspension solution is extremely important. Controlling the stability of the solutions is done through their zeta value. Many studies have shown that increasing the zeta potential increases the stability of the solution, leading to increased absorption of metal nanoparticles for seeds/seedlings. Thereby stimulating germination, enhancing resistance for seedlings, increasing the growth and development of crops.

For each different metal, the content in the solution is different, the ultrasonic vibration time is different so their zeta energy potential is different. To select the optimal ultrasonic vibration time and particle content for each type of metal nanoparticle, we examined the effects of ultrasonic vibration time and particle content on the zeta potential of the suspension solution of metal nanoparticles. The zeta potential of the suspension solution was measured using the Zeta-Nanosizer ZS machine. The results showed that without ultrasonic vibration, the absolute value of the zeta potential of the $Fe^0$, $Cu^0$, $Co^0$ nanoparticle solution was lower and much closer to zero than the solution that had been ultrasonically vibrated. At that time, with the naked eye, it could be seen that the particles tended to cluster and the solution had not yet formed a suspension. Thus, to produce a stable metal nanoparticle suspension solution, we chose the ultrasonic vibration times of the metal nanoparticle solution that gave the largest absolute value of the zeta potential. So the ultrasonic vibration time of the selected nano suspension solutions is: nano $Fe^0$ is 20 minutes, nano $Cu^0$ is 20 minutes and nano $Co^0$ is 30 minutes.

## 3.3. Results of evaluating the effects of metal nanoparticles $Fe^0$, $Cu^0$ , $Co^0$ on corn, ginger, wheat, and barley plants

### *3.3.1. Results for corn*

The purpose of the study is to evaluate the growth ability, chlorophyll content, flavonoid biological compounds including anthocyanin of corn plants, this is to clarify the mechanism of action of metal nanoparticles on each type of plant cell and determine the type of metal nanoparticles with the content Its optimum affects drought resistance, growth and yield of corn plants .

The experiment included 11 formulas shown in Table 3.1 with 3 types of metal nanoparticles at 3 different concentrations and 2 control formulas including formula 1 without treatment, i.e. direct seeding, and formula 2 treated with water respectively. The experiment was conducted in 2 steps. The first step was done in the laboratory. The second step was a field production test.

***Table 3.1 .*** *Experimental* formula

| STT | Recipe |
|---|---|
| 1 | DC1 (Control, no treatment ) |
| 2 | DC2 (Control treated with water) |
| 3 | Fe CT1 ( nano Fe concentration 5 mg/ l) |
| 4 | Fe CT2 ( nano Fe concentration 4 mg/ l) |
| 5 | Fe CT3 ( nano Fe concentration 3 mg/ l) |
| 6 | Cu CT1 ( nano Cu concentration 5 mg/ l) |
| 7 | Cu CT2 ( nano Cu concentration 4 mg/ l) |
| 8 | Cu CT3 ( nano Cu concentration 3 mg/ l) |
| 9 | Co CT1 ( nano Co concentration 5 mg/ l) |
| 10 | Co CT2 ( nano Co concentration 4 mg/ l) |
| 11 | Co CT3 ( nano Co concentration 3 mg/ l) |

*3.3.1.1. Evaluation of the effect of treating corn seeds with metal nanoparticles in a nursery-scale experiment*

When surveying and evaluating the effects of treating corn seeds with metal nanoparticles in a nursery-scale experiment . The effects of treating corn seeds with metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$ on germination , growth and development and evaluating the chlorophyll and anthocyanin content under nano-particle treatment conditions in young corn plants were investigated .

results evaluated the growth and development of corn plants when seeds were treated with 3 types of nano $Fe^0$, $Cu^0$ and $Co^0$ , through evaluation, it was shown that seeds treated with metal nanoparticles grew faster and more evenly, in which the impact of nano $Cu^0$ and $Co^0$ was stronger than nano

$Fe^0$ in stem growth; on the contrary, nano $Fe^0$ enhanced root growth better than the other two types of nano.

All three metal nanoparticles enhanced the ability to synthesize chlorophyll and anthocyanin, in which, nano $Fe^0$ showed the highest role in enhancing chlorophyll; on the contrary, the treatment formula with $Cu^0$ and $Co^0$ at a concentration of 4mg/l gave the highest result in enhancing anthocyanin content .

Through the results of evaluating the effects of metal nanoparticles on germination rate, growth and development ability of corn plants and the ability to enhance anthocyanin biosynthesis. It was found that nano $Cu^0$ at a concentration of 4mg/l gave the best results. Therefore, I continued to study the effects of nano $Cu^0$ on the growth ability of corn plants under artificial drought conditions.

Evaluation of corn plant growth when treated with Cu nanoparticles 0.4 mg/l under normal conditions and artificial drought conditions. I evaluated some biochemical indicators such as chlorophyll and carotenoid content, anthocyanin content, SOD and APX enzyme activities in corn leaves, and yield components at 7 days, 14 days and 21 days after drought.

For chlorophyll and carotenoid content. The results showed that corn plants treated with nano Cu had higher chlorophyll and carotenoid content than the control under drought conditions at 7, 14, and 21 days after drought. Carotenoids are known as chlorophyll protectors. Carotenoid content in control plants under drought conditions decreased by 81, 64, and 53% at 7, 14, and 21 days after drought treatment, respectively. Meanwhile, plants treated with nano Cu had carotenoid content decreased by 79, 81, and 64% at 7, 14, and 21 days after drought treatment. The high carotenoid content in plants treated with nano Cu under drought conditions contributed to protecting the plants from chlorophyll degradation caused by drought conditions. In addition, the higher chlorophyll content in corn plants treated with nano Cu may also contribute to the less biomass loss compared to the control.

Evaluation of the increase in anthocyanin content caused by drought showed that both groups treated with nano $Cu^0$ and the control had increased anthocyanin content compared to the untreated sample. The anthocyanin content after 21 days of drought also had differences between the treatment groups. Under normal conditions without drought, corn plants treated with nano Cu and the control had similar anthocyanin content (the difference was not statistically significant). On the contrary, under 21 days of drought treatment, the anthocyanin content in corn plants treated with nano Cu was higher (1.16 times) than the control with a significant difference. Similar to the time point 14 days after drought, evaluation of the accumulation of anthocyanin caused by drought in corn plants treated with nano Cu and the control both showed a significant increase when compared to the corresponding non-drought samples. This result demonstrates that increasing anthocyanin content is one of the adaptive mechanisms of plants in response to drought conditions.

The results of enzyme activity measurements of corn leaves under normal conditions and artificial drought conditions showed that plants treated with nano $Cu^0$ had higher SOD and APX enzyme activities than the control. SOD is a particularly stable enzyme that can convert destructive superoxide radicals into a less dangerous form, hydrogen peroxide. The increased activity of SOD under drought conditions helped corn plants treated with nano copper reduce the amount of superoxide accumulated in the plant, thereby helping the plant adapt better to drought conditions. Similarly, along with the increase in SOD enzyme activity, the analysis of APX enzyme activity also showed an increase in enzyme activity under drought conditions, thereby helping the plant reduce the amount of free oxidants in the plant. APX is known to be an enzyme involved in the conversion of hydrogen peroxide into water and standard oxygen. Increased APX activity reduces the amount of accumulated hydrogen peroxide, thereby helping the plant respond better to drought through the detoxification mechanism caused by free oxidants.

Along with the increased carotenoid content (non-antioxidant), the increased activity of antioxidant enzymes such as SOD and APX helps plants to be better protected under drought conditions, as shown by the decrease and decomposition of chlorophyll caused by drought.

Compared with non-drought-treated plants, corn plants treated with nano Cu under drought conditions showed a 30% reduction in the number of grains/plant and a 20% reduction in grain weight (grain yield/plant). Meanwhile, the control plants under drought conditions showed a 77% reduction in the number of grains/plant and a 61% reduction in grain yield/plant. This result shows the potential of applying copper nanoparticles in maintaining corn yield under drought conditions. The grain yield results are also consistent with the maintenance of higher chlorophyll content in corn plants treated with nano copper under drought conditions compared with the corresponding control plants.

*3.3.1.2. Effect of treatment with metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$ on corn growth through field test results*

The purpose of the experiment was to evaluate the growth, development and yield of corn when using metal nanoparticles to treat seeds. The experiments were carried out on a sloping alluvial land with light loam soil characteristics in Chieng Sung commune, Mai Son district, Son La province with the LVN10 corn variety.

Survey to evaluate the effects of seed treatment with metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$ on the growth of maize plants at young stage , mature stage , drought resistance , and pest resistance. and to the factors that make up the yield and productivity of corn plants . The results showed that seeds treated with metal nanoparticles help corn plants grow faster and more evenly than the control, the pollen release and silking time is also earlier, the corn plants' ability to resist drought is better and that leads to better yield.

### 3.3.2. Results for ginger plants

The effects of treating ginger tubers with nano metals $Cu^0$ , $Fe^0$ , $Co^0$ on the growth time and growth indicators of buffalo ginger plants were investigated , including: Evaluation of the effects of nano metals on height, branching ability , leaf length, width, harvested ginger yield and harvested ginger quality of buffalo ginger plants.

The results showed that for the tubers treated with metal nanoparticles, we saw that the ginger plants in the group treated with nano $Fe^0$ had leaves 3-4 days earlier and tillered 1-2 days earlier than the control; those treated with nano $Co^0$ had leaves 2-3 days earlier and tillered 1-2 days earlier than the control. In particular, treatment with nano $Fe^0$ shortened the harvest time by about 5 days. Evaluation of harvested ginger yield showed that:

- Treatment with nano $Cu^0$ at a concentration of 500 mg/ha gave a high yield exceeding 14.2% compared to the control.
- Buffalo ginger treated with nano $Fe^0$ at a content of 400 mg/ha gave a high yield 30.8% higher than the control .
- Treatment with nano $Co^0$ at a concentration of 300 mg/ha gave the highest yield, 45.02% higher than the control.

### *3.3.3. Effects of metal nanoparticles on wheat and barley plants under temperate climate conditions*

The aim of this study was to investigate the effects of metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$ on the growth and development of wheat and barley plants in temperate climates when seeds were treated before planting. The experiment was conducted at the Institute of Experimental Botany of the National Academy of Sciences of Belarus.

effect of nano metals on the development of antifungal properties of wheat and barley seeds was investigated . The effect of pre-planting seed treatments on yield and plant structural indices was investigated.

The results of plant structure analysis showed that nano-treatment had a significant effect on stems and seeds. The most significant improvement was observed for $Fe^0$ and $Co^0$ metal nanoparticles . These metal nanoparticles increased the average stem weight by 20-60%, and the ear weight by 20-50%. Seed treatment with 0.5 mg/kg $Co^0$ nano gave the best results.

## CONCLUDE

Based on the research results of the thesis, some conclusions can be drawn as follows:

**1.** By the method of reduction by newly generated hydrogen, the physical and chemical properties of nano materials $Fe^0$, $Cu^0$, $Co^0$ were successfully fabricated and investigated . In which:

$Fe^0$ was produced from $Fe_2O_3$ at a reduction reaction temperature of 400°C , reaction time of 90 minutes , average particle size of 58.76nm, purity of 99.67%.

$Cu^0$ was produced from CuO at a reduction reaction temperature of 400 °C, reaction time of 60 minutes, average particle size of 58.94nm, purity of 99.60%.

$Co^0$ was produced from $Co_3O_4$ at a reduction reaction temperature of 500 °C, reaction time of 60 minutes, average particle size of 71.75nm, purity of 99.71%.

**2.** The influence of metal nano content and ultrasound time on the zeta potential of the seed treatment solution has been investigated and a suitable process for treating different types of seeds has been proposed. Specifically:

nano $Fe^0$ suspension solution : Suitable ultrasonic vibration time for each concentration of 3mg/l, 4mg/l, 5mg/l is 20, 10, 20 minutes respectively.

nano $Cu^0$ suspension solution : Suitable ultrasonic vibration time for each concentration of 3mg/l, 4mg/l, 5mg/l is 20 minutes.

nano $Co^0$ suspension solution : Suitable ultrasonic vibration time for each concentration of 3mg/l, 4mg/l, 5mg/l is 20, 30, 30 minutes respectively.

**3.** The ability to stimulate growth during the germination stage, stem, root, leaf development, and increase yield of corn, ginger, wheat, and barley after treatment with metal nanoparticles $Fe^0$, $Cu^0$, and $Co^0$ has been studied and evaluated. Specifically as follows :

***+ For corn:***

- Seeds treated with metal nanoparticles $Fe^0$, $Cu^0$, $Co^0$ help corn plants grow faster and more evenly than the control, and corn plants have better drought resistance.

- Clarifying the mechanism of the impact of nano metals on the growth and development and drought resistance of corn plants, especially when treated with nano $Cu^{0.}$ Seed treatment with nano $Cu^0$ at a concentration of 4 mg/ l gave the highest yield (74.66 tons/ha), exceeding the control (61.69 tons/ha) by 21.02%.

- The issue of post-harvest product quality is evaluated through the starch content in the finished corn. The results for the starch content in corn show that: The starch content in the treatment formula with nano $Co^0$ , $Fe^0$ is higher than the control. Although the starch content in the finished corn is not higher than the control, Nano $Cu^0$ compensates by increasing the yield beyond the control.

- Environmental and food safety issues were assessed through the residual metal content of $Fe^0$ , $Cu^0$ , $Co^0$ in finished corn. The results showed that the seed treatment process did not change much the metal content in finished corn, even decreased compared to the control or below the detection threshold of the measurement. The metal concentration in all corn samples was much lower than the permissible limits of the World Health Organization WHO.

***+ For ginger:***

For tubers treated with metal nanoparticles, we see that ginger plants in the group treated with nano $Fe^0$ have leaves 3-4 days earlier and tiller 1-2 days earlier than the control; those treated with nano $Co^0$ have leaves 2-3 days earlier and tiller 1-2 days earlier than the control. In particular, treatment with nano $Fe^0$ shortens the harvest time by about 5 days. Evaluation of harvested ginger yield shows that:

- Treatment with nano $Cu^0$ at a concentration of 500 mg/ha gave a high yield exceeding 14.2% compared to the control.

- Buffalo ginger treated with nano $Fe^0$ at a content of 400 mg/ha gave a high yield 30.8% higher than the control.

- Treatment with nano $Co^0$ at a concentration of 300 mg/ha gave the highest yield, 45.02% higher than the control.

- The residual metal content of $Fe^0$ , $Cu^0$ , $Co^0$ in ginger after harvest showed that the content of nano $Fe^0$ , $Cu^0$ was low and lower than the control. The content of nano $Co^0$ was below the detection threshold of the measurement.

- The issue of post-harvest product quality was evaluated through the content of 6-gingerol and 6-shogaol in ginger essential oil. The results showed that the group using nano $Cu^0$ to treat ginger tubers had quite low levels of 6-gingerol and 6-shogaol in ginger essential oil, 1.7-3.8 times lower than the control. Meanwhile, nano $Fe^0$, $Co^0$ gave higher results than the control.

**+ *For wheat and barley:***

Analysis of plant structure showed that nanoparticle treatment had significant effects on stems and seeds. The most significant improvement was observed for $Fe^0$ and $Co^0$ metal nanoparticles. These metal nanoparticles increased the average stem weight by 20-60%, and the ear weight by 20-50%. Seed treatment with 0.5 mg/kg $Co^0$ nanoparticle gave the best results.

**4.** Through the results of testing with different plants, in different climate and soil conditions, it shows that: Each type of plant, regardless of climate and soil conditions, can cause growth stimulation effects by metal nanoparticles after seed treatment. However, each type of metal nano particles can only have a positive effect on a certain type of plant, at a certain concentration.

## NOVELTY OF THE THESIS

1. Development of a Novel Synthesis Method: Developed and clarified the theoretical basis and experimental conditions for the method of preparing non-powdered covalent metal nanocrystals ($Fe^0$, $Cu^0$, $Co^0$) from corresponding oxides and hydroxides by the reduction method by hydrogen generated from water electrolysis.

2. Established the fabrication conditions and characteristic parameters for the suspension solution of each type of metal nano ($Fe^0$, $Cu^0$, $Co^0$) to treat corn, wheat, barley/ginger seed before planting.

3. Indicated the mechanism of action and biological activity of metal nano on the growth and development of corn after seed treatment through the survey of important pigments such as chlorophyll and anthocyane content. Clarifying the drought tolerance mechanism of corn based on the impact of nano $Cu^0$ particles on enzyme activity (APX, SOD) of the plant.

4. It has been shown that treating seeds with nano metals gives positive results for many crops in different soil and climate conditions. However, each nano metal has a positive impact on each crop. In tropical climate conditions (Vietnam), treatment with nano $Cu^0$ with a content of 80mg/ha increased corn yield by 21.02%, nano $Co^0$ with a content of 300mg/ha increased ginger yield by 45.02%. In temperate climate conditions (Belarus), treatment with nano $Co^0$ at a concentration of 0.5 mg/kg of barley varieties increased the weight of rice panicles by 1.2-1.5 times compared to the control. The biosafety of seed treatment with metal nanoparticles was also demonstrated through the assessment of metal nanoparticle residues in harvested products, which were all below the limits set by the WHO.