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Green Synthesized Co_3O_4 Nanostructures: Dual-Functional Materials for Nano-Agricultural Applications (Growth Promotion and Disease Control)

Ramin Karimian^{1*}

¹Chemical Injuries Research Center, Systems Biology and Poisonings Institute, Baqiyatallah University of Medical Sciences, Tehran, Iran.

*Corresponding author Email: karimian.r@gmail.com

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Abstract

Background: The unique properties of cobalt oxide (Co_3O_4) nanostructures, particularly their antimicrobial and catalytic activities, make them promising candidates for nano-agricultural applications. However, many synthesis methods require complex conditions, limiting their practical use. This study presents a facile green synthesis of Co_3O_4 nanotubes using a reverse micelle system and evaluates their dual functionality as plant growth promoters and antibacterial agents. **Method & Material:** Co_3O_4 nanotubes were synthesized via a reverse micelle template method using cobalt(II) chloride as a precursor, purified soybean oil as the organic phase. The resulting nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The agricultural performance evaluation of these nanostructures in research showed that their application leads to significant improvement in growth parameters including shoot length, root length and dry weight of plants and reduction in the percentage of infected leaf area. **Result:** The synthesized Co_3O_4 nanotubes exhibited a uniform morphology with an average length of 261 nm and an outer diameter of 58 nm. Application of these nanotubes significantly enhanced plant growth parameters, including shoot length, root length, and dry weight. In addition, they showed strong antibacterial activity and reduced the diseased leaf area in plants by forming biofilms. **Conclusion:** The green-synthesized Co_3O_4 nanotubes serve as effective dual-functional nanomaterials, promoting plant growth and providing protection against bacterial pathogens. Their simple synthesis method and high efficacy make them suitable for sustainable agricultural practices, offering a promising strategy to enhance crop productivity and disease management.

Keywords: Co_3O_4 nanotube, Green Synthesis, Reverse Micelle, Plant Growth, Disease Control.

1. Introduction

In recent years, there has been increasing interest in developing low dimensional nanostructured materials such as nanotubes and nanorods due to their potential technological applications in nanoscale devices. It has become evident that their properties are highly dependent on their size and shape. Consequently, a primary challenge in nanocrystal synthesis is controlling not only the crystal size but also the morphology (1,2).

Various methods have been developed to produce desired nanostructural materials, including electrodeposition (3,4), molecular beam epitaxy (MBE) (5), sol-gel processing (6), homogeneous precipitation (7), chemical reactions (8), hydrothermal methods (9), and deposition on a support (10). Co_3O_4 is an important functional material with a wide range of technological applications, such as in heterogeneous catalysts, anode materials for Li-ion rechargeable batteries, solid-state sensors, and magnetic and optical devices. Owing to the significant influence of particle size and morphology on material properties, the controlled preparation of Co_3O_4 particles with specific characteristics is a key research objective. To date, Co_3O_4 particles with various morphologies, such as nanotubes and nanorods (11), nanocubes (12), nanosheets (13) and hollow nanospheres (14) have been successfully prepared.

Although diverse Co_3O_4 nanostructures have been synthesized, many preparation methods require complex techniques or rigorous conditions. Herein, we describe a

simple method for generating Co_3O_4 nanotubes. In our experiments, Co_3O_4 nanotubes were obtained using nano- and micro-reverse micelles with basic cobalt (II) chloride as a precursor and purified soybean oil as the organic phase.

A micelle is an aggregate of surfactant molecules dispersed in a liquid colloid. In an aqueous solution, a typical micelle forms with hydrophilic head regions in contact with the surrounding solvent, sequestering the hydrophobic tail regions in the center. This structure results from the packing behavior of single-tail lipids in a bilayer. The difficulty of filling all the interior volume of a bilayer while accommodating the area per head group dictated by lipid head hydration leads to micelle formation. The type described here is known as a reverse micelle. The shape and size of a micelle are functions of the molecular geometry of its surfactant molecules and solution conditions, such as surfactant concentration, temperature, pH, and ionic strength. This article describes the use of organic anionic surfactants to stabilize reverse (water-in-oil) micelles containing water-soluble transition metal salts.

Cobalt oxide nanoparticles (Co_3O_4 NPs) have been recognized as effective agents for improving plant growth and controlling disease. Their unique magnetic, catalytic, and antimicrobial properties have led to wide agricultural applications. These nanoparticles enhance the growth of model plants like *Arabidopsis* and act as nano-pesticides against bacterial pathogens such as *Xanthomonas oryzae*. Studies show that their application increases stem length, root length, and plant

dry weight, alongside a significant improvement in the photochemical efficiency of photosystem II (PSII). Furthermore, they inhibit pathogenic bacterial growth and biofilm formation, reducing the diseased leaf area in rice plants. These protective qualities make Co_3O_4 NPs an attractive option for sustainable agriculture. This study demonstrates that green-synthesized cobalt oxide nanoparticles can produce non-toxic, environmentally friendly nanomaterials for agricultural use, contributing to improved plant health and increased crop yield (15-22).

2. Materials and Methods

All chemicals, including CoCl_2 , NaOH , and Tween 80, and solvents were purchased in high purity from Merck and used as received without further purification. Reaction monitoring and purity determination were performed using thin-layer chromatography (TLC) on silica gel plates (Polygram SILG/UV 254). X-ray diffraction (XRD) analysis was conducted on a Philips Analytical XPERT diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electron microscopy (SEM) was performed using a PHILIPS XL-30 microscope operating at 30 kV. Transmission electron microscopy (TEM) was carried out on a Zeiss EM10C instrument operating at 80 kV.

Experimental Method

Nanotubes were synthesized using the following procedure: A solution (Solution A) was first prepared by adding a mixture of 0.30 g of CoCl_2 in 1 mL of water and 4% Tween 80 into 30 mL of purified soybean oil. This was emulsified under mechanical stirring at 2000 rpm until a nearly clear emulsion was obtained. Next, 0.16 g of NaOH dissolved in 1.5 mL of water was added to Solution A and stirred at 2000 rpm for 2 h at room temperature. The resulting reaction mixture was then filtered, and the collected precipitate was washed three times with 300 mL of deionized water. The washed material was calcined in an electronic oven at 200°C for 1 h.

The phase composition of the resulting powder was characterized by X-ray diffraction (XRD) using a Philips Analytical XPERT diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Data were collected with a MINIPROP detector operating at 40 kV and 40 mA. Scans were performed over a 2θ range of 5° to 79° with a step size of 0.04° and a counting time of 0.8 s per step. Crystallographic data were processed using the PC-APD Diffraction software. The surface morphology of the specimens was examined using a scanning electron microscope (SEM, Philips XL-30). The ordered nanostructure of the Co_3O_4 was further confirmed by transmission electron microscopy (TEM, Philips KV-120).

3. Results

Figure 1 shows scanning electron microscopy (SEM) images of the synthesized Co_3O_4 nanotubes, indicating a homogeneous size distribution and high product purity. The nanotubes are arranged in a parallel and well-ordered manner. Although some nanotubes fractured during sample preparation, the intact ones appear straight

and uniform along their lengths. The morphology and structure of individual nanotubes were further characterized using transmission electron microscopy (TEM). The TEM image (Fig. 2) confirms the single-nanotube morphology. The nanotubes have lengths ranging from 200 to 550 nm, with an average length of approximately 261 nm, and a diameter of about 58 nm. Each nanotube is straight and uniform along its entire length, with an outer diameter of $\sim 261 \text{ nm}$ and a wall thickness of $\sim 10 \text{ nm}$. The synthesized cobalt oxide nanotubes exhibit a well-defined structure and remain stable in hydrocarbon solvents against air oxidation. Figure 3 shows a typical X-ray powder diffraction (XRD) pattern of the product. All diffraction peaks can be indexed to the cubic phase of Co_3O_4 , consistent with the standard JCPDS card no. 43-1003. The calculated lattice constant ($a = 8.08 \text{ \AA}$) agrees with the standard value for bulk Co_3O_4 . Using the Scherrer equation, the average crystallite size of the nanoparticles composing the nanotubes was estimated to be approximately 280 nm.

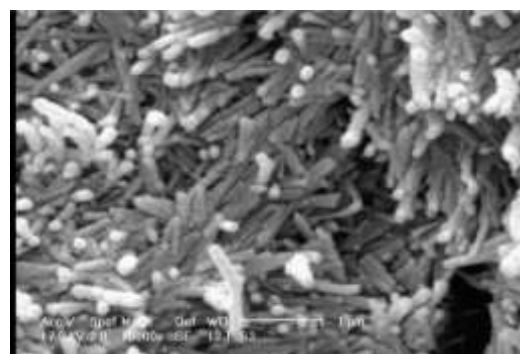


Fig. 1. SEM image of the Co_3O_4 nanotube.

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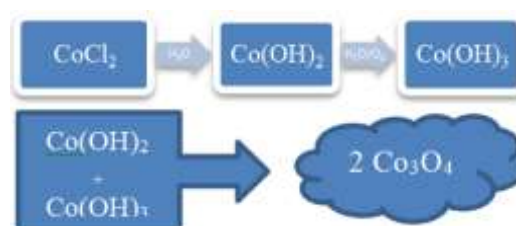
Fig. 2. TEM image of the Co_3O_4 nanotube.

[Image not available in the source file]

Fig. 3. XRD pattern of the Co_3O_4 nanotube.

4. Discussion

The synthesis of Co_3O_4 in this process is proposed to follow a two-step mechanism. Initially, the dissolution of CoCl_2 in water leads to the formation of $\text{Co}(\text{OH})_2$. This compound is then partially oxidized by environmental oxygen to form $\text{Co}(\text{OH})_3$. In the second step, these hydroxide species co-precipitate under basic conditions, resulting in the formation of Co_3O_4 nanostructures. This reaction pathway is summarized in the following chemical equations:



Scheme 1. Proposed two-step reaction pathway for the formation of Co_3O_4 from CoCl_2 .

This work provides valuable insights into the design of eco-friendly nanostructures for agrochemical applications. The simplicity of the synthesis, the use of low-cost and non-toxic materials, and the efficacy of the resulting nanotubes make them a highly attractive alternative to conventional chemical agents. Future studies should focus on field trials to validate these findings under real-world conditions, along with detailed investigations into the long-term environmental fate and safety of these nanomaterials to ensure their sustainable and safe integration into agricultural practices.

5. Conclusion

This study successfully demonstrates a facile and efficient reverse micelle-based method for the green synthesis of well-defined Co_3O_4 nanotubes using cobalt chloride, Tween 80, and purified soybean oil. The synthesized nanotubes exhibited a uniform morphology with an average length of 261 nm and diameter of 58 nm, and were characterized by high purity and crystallinity.

Beyond the synthetic achievement, this research highlights the significant potential of these green-synthesized Co_3O_4 nanotubes as dual-functional nanomaterials in sustainable agriculture. Their application offers a promising strategy for enhancing plant growth and controlling bacterial diseases simultaneously. The nanotubes function effectively as a nano-stimulant, improving key growth parameters such as root and shoot length and biomass, likely through the enhancement of photosynthetic efficiency. In addition, they inhibit the growth of bacteria and reduce the incidence of disease in plants.

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