Development of Cobalt Nickel Doped TiO₂ Nanowires as Efficient Photocatalysts for Removal of Tartrazine Dyes

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Abstract: Tartrazine is a yellow synthetic dye that is widely used as a coloring agent in food and beverage products. However, the safety of this chemical compound is still a concern due to potential health risks such as allergic reactions, hyperactive behavior in children, increased risk of cancer and other negative impacts. This research aim to introduces a new approach to reduce the concentration of tartrazine dye using cobalt and nickel doped TiO₂ nanowires. Cobalt- and nickel-doped TiO₂ nanowires were synthesized by a hydrothermal method, followed by thermal treatment at 270°C, and then used in a photocatalytic reactor using UV irradiation to facilitate the reduction of tartrazine concentration. Material characterization was carried out to determine the morphology and crystallinity of the photocatalyst which is effective in reducing the absorption of tartrazine solution. The photocatalytic degradation experiment demonstrates the ability of the synthesized material as a photocatalyst, effectively reducing the absorbance of tartrazine solution, a commonly used food coloring. This finding promises significant progress in the development of sustainable food safety strategies by offering a dye degradation method.

Keywords: Cobalt; Degradation; Dye food; Nickel; Photocatalytic; Tartrazine; TiO₂ nanowire

Introduction

Tartrazine is a synthetic dye that is commonly used in foods and beverages to impart a bright yellow color. While many countries allow its use in regulated quantities, there are concerns regarding the potential hazards associated with this coloring agent, including allergic reactions such as itching, skin rashes, swelling of the lips or face, breathing difficulties, and even anaphylaxis.; behavioral disturbances, as tartrazine consumption has been linked to exacerbated hyperactivity symptoms in children, particularly those with attention deficit hyperactivity disorder (ADHD); mental health implications, in addition to the association between tartrazine consumption and anxiety and depression in adults; and general health impacts, including immune system disorders and digestive disorders (Laura et al., 2019; Weisbrod et al., 2023). Safety thresholds for the use of tartrazine in food and beverages have been established by various food regulatory authorities worldwide. These standards are based on risk evaluations carried out by bodies such as the Food and Drug Administration (FDA) in the United States, the European Food Safety Authority (EFSA) in the European Union, and the National Agency for Food and Drug Monitoring (BPOM) in Indonesia (Commissioner, 2024).

In general, the safe threshold for using tartrazine is set as Acceptable Daily Intake (ADI), which is the estimated amount of tartrazine that can be consumed every day without causing negative effects on health. According to EFSA, the ADI for tartrazine is 7.5 mg/kg

body weight per day, while the FDA in America allows the use of tartrazine in food and drinks with a maximum limit of 100 mg/kg food ingredients (Dey et al., 2022). It is important to note that these safe thresholds are based on a scientific assessment of the health risks associated with tartrazine consumption in the general population, including vulnerable groups such as children and pregnant women (Amin et al., 2018). However, individuals who suffer from allergies or sensitivities to tartrazine should carefully monitor the amount in their food and drink consumption.

Several methods have been explored to reduce the impact of tartrazine, including techniques to eliminate or reduce its content in foods, as well as the development of safer and more natural alternative dyes. Removal of tartrazine from food products requires serious attention, especially for individuals who are allergic or sensitive to this food coloring. Several studies have identified and evaluated various techniques for removing tartrazine from food products, including: Separation methods using Chromatographic Techniques, Techniques such as column chromatography or liquid-gas chromatography (LC-GC) separate tartrazine from other food components based on differences in tphysicochemical properties, such as particle size, polarity, or affinity to the separation phase (Sha et al., 2014). Adsorption with Activated Carbon, Activated carbon is an effective adsorbent material for removing colorants from solutions. Several studies have shown that treating food products with activated carbon can reduce tartrazine content (Brice et al., 2021; Joshiba et al., 2022). Enzymatic Treatment, This approach involves the enzymatic degradation of tartrazine into simpler and less colored compounds. For example, amylase enzymes have been used to modify the molecular structure of tartrazine, producing less allergenic compounds (Ameur et al., 2019). Physical methods, Techniques such as annealing, drying, or heating have also been investigated for their potential to influence tartrazine content in food products (Silva et al., 2022).

However, these methods have limitations. Chromatographic methods are not considered sufficiently efficient for direct application, Enzymatic methods naturally require large amounts of enzymes, and physical methods such as heating cannot avoid affecting the organoleptic and nutritional properties of food. In addition, the adsorption method will produce new waste after the adsorbed dye accumulates on the adsorbent.

Photocatalytic degradation of tartrazine from food products is an approach gaining significant research focus in recent years. Photocatalytic reactions involve the use of light-activated catalysts, either UV light or sunlight, to degrade or change dye compounds in solutions or food matrices (Khan et al., 2023; Pavel et al., 2023). UV light initiates the formation of electron-hole pairs on the catalyst surface, then participates in the photocatalytic oxidation reaction (Misriyani et al., 2015). Tartrazine in food reacts with the ionized oxygen and hydroxyl radicals produced by the photocatalytic catalyst (M. Li et al., 2014; Zazouli et al., 2017; Zhou et al., 2019). This reaction causes the degradation of tartrazine into simpler or less dangerous compounds.

Cobalt (Co) and nickel (Ni) doping on TiO_2 has several roles in improving photocatalytic performance, including: Increase Light utilization Efficiency: Cobalt and nickel doping can modify the structure and electronic properties of TiO_2, resulting in better light absorption over a wider spectrum range (Nazir et al., 2021); Enhances the Formation of Electron-Hole Pairs: Cobalt and nickel can act as additional impurities or reaction sites in the TiO_2 crystal structure, facilitating the formation of electron-hole pairs that participate in redox reactions and promote the degradation of target organic compounds (Misriyani et al., 2020; X. Zhang et al., 2021); Improving Electron Transfer Efficiency: Cobalt and nickel doping can increase the efficiency of electron transfer from TiO_2 to target compounds, such as tartrazine (Jensen et al., 2015; Jiang et al., 2015; Subramanian et al., 2008). This can accelerate the photocatalytic reaction and enhance the catalytic activity in removing organic pollutants from food matrices; Enhancing Anatase Phase Stability: Cobalt and nickel doping can influence the stability of the TiO_2 crystal phases, particularly the anatase phase, which exhibits higher photocatalytic activity (Barakat et al., 2005; Katherine et al., 2023); Cobalt and nickel doping can maintain the crystal structure of anatase in TiO_2, which is important for maintaining long-term photocatalytic performance; Increasing Reaction Selectivity: Cobalt and nickel doping can modify the surface characteristics of TiO_2, affecting the adsorption and interaction between target compounds and the catalyst (R. Li et al., 2020). This can lead to improved selectivity in photocatalytic reactions, reducing the formation of undesired side products and enhancing the efficiency of target organic compound degradation.

Cobalt and nickel dopants into TiO_2 are expected to improve the photocatalytic performance of TiO_2, thereby expanding the potential application in organic waste processing, including the degradation of tartrazine in food. This study carried out the synthesis of cobalt and nickel doped TiO_2 nanowires using the hydrothermal method. This technique is recognized as a general approach for the fabrication of nanomaterial structures characterized by large surface area, favorable photocatalytic properties, and wide utility in the fields of photocatalysis and electronics. This research

introduces the development of cobalt and nickel doped TiO_2 nanowires specifically designed for efficient removal of tartrazine dyes. The combination of dopant and target application suggests a new approach in the field of photocatalytic dye removal.

Method

In order to investigate the photocatalytic degradation of tartrazine dye, this study synthesized Ni-Co doped TiO_2 nanowires. Commercially available Aeroxide P25 TiO_2 powder served as the base material. Sodium hydroxide solution transformed these nanoparticles into sodium titanate nanowires through hydrothermal treatment at 240°C for 72 hours. Subsequently, nickel and cobalt ions were incorporated into the sodium titanate nanowires creating the desired Ni-Co doped TiO_2 nanowires. A combination of magnetic stirring, ultrasonication, and controlled hydrothermal treatment facilitated the formation of these nanowires. To analyze the characteristics and performance of the synthesized material, X-ray diffraction (XRD) was used to determine the crystal structure, while scanning electron microscopy (SEM) examined the morphology and surface features of the nanowires. Finally, UV-visible spectrophotometry played a twofold role: assessing the band gap energy of the nanowires and analyzing their photocatalytic activity in degrading a tartrazine dye solution.

Materials and Methods

In this study, the materials employed were Aeroxide P25 titanium dioxide (TiO_2) powder, sodium hydroxide pellets (NaOH) procured from Macron Fine Chemicals, nickel(II) chloride, cobalt(II) chloride, and Tartrazine Acid Yellow 23.

The crystallinity of iron ions doped TiO_2 nanowires was characterized using an X-ray diffractometer (Rigaku MiniFlex II). A scanning electron microscope (TESCAN VEGA) and an optical microscope (Olympus BX41) were utilized to map the image and morphology of the samples, with the scanning electron microscopy operated at 10 kV. A Shimadzu UV-1280 UV-Vis spectrophotometer was employed to determine the band gap energy and analyze the photocatalytic activity. The hydrothermal synthesis was performed in an autoclave (Parr USA).

Procedure
Synthesis of Ni Co Doped TiO$_2$ Nanowire

First, sodium titanate nanowires were synthesized via the hydrothermal route, following the protocol reported in a previous study (Ryan, 2014). Specifically, 0.125 g of TiO_2 nanoparticles were mixed with a 10 M

alkaline solution and subjected to magnetic stirring for 2 hours, coupled with ultrasonication for 15 minutes to obtain a milky white suspension. The suspension was then transferred to a Teflon-lined autoclave and hydrothermally treated at 240°C for 72 hours. After cooling to room temperature, the samples were collected and rigorously washed with distilled water until a neutral pH was achieved, yielding the desired sodium titanate nanowires. The synthesis of Ni^{2+} and Co^{2+} cations doped TiO_2 nanowires involved incorporating nickel and cobalt powders into the sodium titanate nanowires at 5 molar ratios of Ti/Ni^{2+} and Ti/Co^{2+}.

The mixture underwent magnetic stirring for 2 hours to obtain a milky homogeneous suspension, followed by ultrasonication for 15 minutes for degassing and an additional 5 minutes of stirring. Subsequently, the suspension was transferred to a Teflon-lined autoclave and subjected to hydrothermal treatment under the aforementioned conditions. The synthesized samples were then prepared for further characterization employing X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM, Philips SEM XL30). These analytical techniques provided insights into the morphology, crystal structure, and chemical composition of the doped nanowires.

Photocatalytic Activity Test

Photocatalytic degradation of tartrazine dye was evaluated using 0.025 g of Ni-Co/TiO_2 catalyst in 10 mL of tartrazine solution with an initial concentration of 50 ppm. The mixture was exposed to UV light for 0.5 hours using an incandescent lamp as the light source for the model. The supernatant was separated by centrifugation, and the absorbance value was analyzed using a UV-visible spectrophotometer. For initial measurements, the UV-Vis spectrophotometer was set to a wavelength suitable for tartrazine, usually around 427 nm. The initial absorption value was recorded as a reference. During the photocatalytic process, a portion of the sample solution is taken and the absorbance is measured using a UV-Vis spectrophotometer. Data analysis involved plotting sample absorbance against time to monitor changes in tartrazine concentrations over time. From this plot, tartrazine degradation and the efficiency of TiO_2 photocatalyst in reducing tartrazine concentration were determined.

Result and Discussion

SEM Analysis

The results of SEM analysis of TiO_2 nanowires doped with cobalt and nickel provide an overview of the morphology and surface structure of the material. Figure 1 shows the structure of long and smooth TiO_2

nanowires with uniform distribution forming aggregates on one side. The formation of aggregates shows that the synthesis and doping process has been successful, compared with undoped TiO_2.
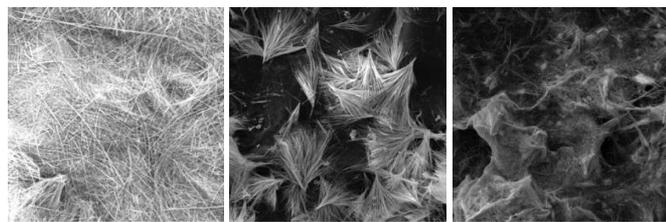

Figure 1. SEM image of a) titanate nanowire; b) cobalt doped TiNW ; and c) nickel doped TiNW

In addition, the cobalt-doped TiO_2 material shows a smoother and uniform nanowire morphology compared to the nickel-doped TiO_2 material. Cobalt can significantly change the morphology of the nanowires into palm leaf-like TiO_2 nanowires. This is because cobalt has a greater influence on changes in the TiO_2 crystal phase, affecting the morphology of the crystal granular and resulting in changes in the size and shape of the granular (Mesilov et al., 2017). Also due to differences in magnetic properties (Singhal et al., 2010; Wang et al., 2015). SEM analysis shows that cobalt and nickel doped TiO_2 nanowires have a uniform morphology with dopant particles distributed on the surface of the nanowires. Nanowire morphology can provide various significant benefits in the development of innovative, healthy and safe food formulations. The long morphology of TiO_2 nanowires can increase the relative surface area of the material, thereby allowing for increased absorption of nutrients, vitamins, or desired additives in food (Biswas et al., 2022; Musial et al., 2020).

The use of nanowires in food industry formulations can increase the physical and chemical stability of products, making them more resistant to storage or processing. The use of TiO_2 nanowires can help reduce microbial contamination of food products and improve food safety (Shehab et al., 2023; Zhu et al., 2018). The unique nanowire morphology can develop new product innovations in the food industry, such as the development of new textures, enhanced nutrient absorption, or the creation of new functional products such as edible films. Edible films containing TiO_2 nanowires can be used as protective coatings for food, helping to reduce microbial contamination and maintain product freshness (Sani et al., 2022; W. Zhang et al., 2022). Edible film containing TiO_2 nanowires is more environmentally friendly than other synthetic materials, because it can decompose naturally after use, thus reducing plastic waste and negative impacts on the environment (Versino et al., 2023).

XRD Analysis

The XRD (X-Ray Diffraction) analysis results of cobalt and nickel-doped TiO_2 nanowires provide information about the crystal structure of these materials. Based on the XRD measurement results shown in Figure 2, the interpretation is as follows:
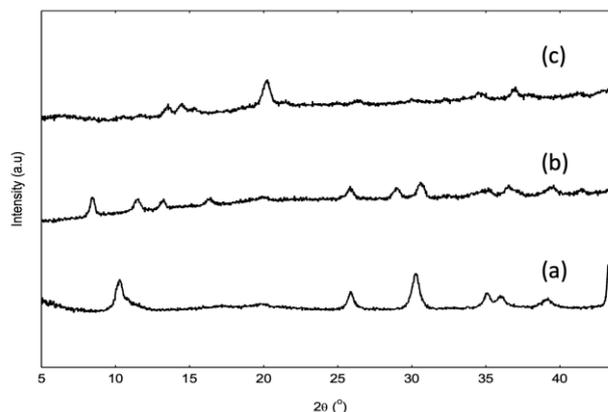

Figure 2. X-Ray diffraction patterns of nanowire (a) TiO_2 Nanowire , (b) Ni-doped TiNW , and (c) Co-doped TiNW

The diffraction peaks observed at 2θ around $25.3°(101)$, $37.9°(004)$, and $48.0°(200)$. This peak indicates the crystal structure of the TiO_2 anatase phase (Dai et al., 2010; Kheamrutai et al., 2008). In the metal ion-doped TiO_2 material, an additional peak appears at around 2θ of $20°$ due to cobalt doping (Nguyen et al., 2020). The changes cause a shift in 2θ or the appearance of a new peak which indicates the formation of a new crystal phase or modification of the TiO_2 crystal structure. The new peak shift is caused by the presence of cobalt in the crystal lattice parameters and the distribution of cobalt in the TiO_2 structure, as well as the substitution of Ti atoms in the TiO_2 structure.

On the other hand, there are no significant peaks for nickel doping. Nickel doping maintains the dominant anatase phase crystal structure at 2θ of $25°$, $30°$, and $37°$ (Rajamannan et al., 2014). New crystal phases due to nickel doping were not found, this confirms that the nickel doping process does not significantly change the crystal structure of TiO_2, as evidenced by the morphology of TiO_2 nanowires observed in SEM analysis.

In XRD (X-Ray Diffraction) analysis of cobalt (Co) and nickel (Ni) doped TiO_2 nanowires, differences in diffraction patterns can be observed depending on the concentration and location of the dopant in the TiO2 structure. Cobalt and nickel dopants can also influence the sharpness and width of the diffraction peaks in the XRD pattern. These changes are due to variations in crystal grain size, crystal distortion, or residual stresses that may occur due to doping.

Photocatalytic Test Results

The photocatalytic performance of tartrazine dye using TiO_2 nanowires will provide an overview of the nanowire's ability to degrade and remove tartrazine dye. The decrease in tartrazine concentration is shown in the figure:
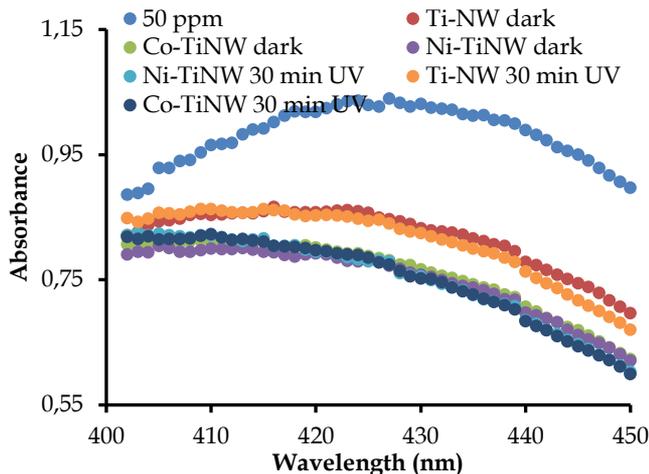

Figure 3. Absorbance test curve of tartrazine dye using cobalt nickel doped TiO_2 nanowire in dark and UV conditions

Figure 3 shows the absorbance measurement curve of the tartrazine solution before and after treatment with doped TiO_2 nanowires at a wavelength of 427 nm. This indicates a decrease in absorbance that is proportional to the decrease in tartrazine concentration in the solution containing TiO_2 nanowires both in the dark and in UV light exposure. This decrease in concentration shows the ability of TiO_2 nanowires to degrade and remove tartrazine into a simpler and safer product. Tartrazine degradation by TiO_2 nanowires may increase with time during the photocatalytic process, possibly following the reaction kinetics increasing with time. At the beginning of the reaction, the TiO_2 surface may need time to become catalytically active, so that the degradation reaction rate may increase gradually. As time passes, intermediate products of the tartrazine degradation reaction may start to accumulate around the TiO_2 nanowires, increasing the contact area between the target compound and the catalyst, which may increase the degradation rate.

The degradation products of tartrazine may be trapped or deposited around the TiO_2 nanowires in the early stages of the reaction. Over time, these degradation products may be released from the catalyst surface, allowing better access to the target compound and increasing degradation efficiency. Finally, the concentration of tartrazine in the solution may decrease due to degradation. Reducing this concentration can reduce the diffusion restriction effect and increase the degradation reaction rate. The photocatalytic process can accelerate secondary reactions that produce radical species such as hydroxyl radicals (•OH) which can also contribute to tartrazine degradation. Over time, the accumulation of these species can enhance the photocatalytic effect and increase the degradation percentage. Varying external conditions such as light intensity, temperature, pH, or catalyst concentration can affect the efficiency of photocatalysis and cause an increase in the percentage of degradation. During the photocatalysis process by TiO_2, tartrazine can undergo oxidation involving a series of complex reactions. tartrazine ($C_{16}H_9N_4Na_3O_9S_2$) is degraded into simpler products through several stages.

The stages in the photocatalysis process with TiO_2 include: Light Absorption, where TiO_2 absorbs light photons, especially UV light, which produces electron-hole pairs (e-, h+) on the surface; Formation of Photocatalytic Radical Species, the electron hole pairs (e-, h+) formed cause a series of photochemical reactions, including the formation of hydroxyl radicals (•OH) from water and dissolved oxygen molecules (Misriyani et al., 2015). Tartrazine is adsorbed onto the TiO_2 surface, allowing direct contact between tartrazine molecules and the resulting ·OH radicals. ·OH radicals react with tartrazine molecules, forming various types of oxidation products. This includes breaking aromatic bonds, breaking sulfonate group bonds, and degradation of the tartrazine structure into simpler compounds. Tartrazine is gradually oxidized and degraded into simpler products, such as smaller organic compounds, carbon dioxide, and water. This process is critical in removing tartrazine from solution, and the ·OH radicals produced by TiO_2 act as the main oxidizing agent in this process.

This entire process occurs on the surface of TiO_2 nanowires under UV light or sunlight and is influenced by various factors such as the type of TiO_2, tartrazine concentration, solution pH, and temperature.

Conclusion

This research successfully developed cobalt nickel doped TiO_2 nanowires using a hydrothermal method. SEM analysis revealed significant morphological changes after doping with cobalt and nickel, suggesting the successful incorporation of dopant elements. XRD patterns confirmed the formation of a typical doped TiO_2 nanowire structure. The photocatalytic degradation experiment demonstrates the ability of the synthesized material as a photocatalyst, effectively reducing the absorbance of tartrazine solution, a commonly used food coloring. The degradation process likely involves the generation of hydroxyl radicals under UV light exposure. This finding provides significant progress in the development of sustainable food safety

by offering a dye removal method using TiO₂ nanowire material.

Author Contributions
Conceptualization, M. Y., I, L. S.; methodology, M. Y.; validation, M. Y. and I.; formal analysis, M. Y.; investigation, M. Y., and L. S.; resources, M. Y. and L. S.; data curation, M. Y.; writing-original draft preparation, M. Y. and I.; writing-review and editing, M. Y.: visualization, M. Y., I. and L. S. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest
The author declares that there is no conflict of interest.

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