Photocatalytic degradation of heavy metal in dairy milk by N-doped ZnO thin film using spray coating technique

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Abstract. Zinc Oxide (ZnO) is a photocatalytic material. N-doped ZnO thin film can reduce heavy metals in milk. In the process, N-doped ZnO thin film photocatalyst is deposited on the glass by spray coating technique. N-doped ZnO thin film was characterized using UV-Vis (Ultraviolet/Visible Spectroscopy), X-Ray Diffraction (XRD) and FTIR (Fourier Transform Infrared). This study aims to investigate the reduction of heavy metals in milk due to N-doped ZnO thin film. In this study, dairy milk was obtained from farms in Central Java. Characterization results show that the band gap of N-doped ZnO thin film is 3.2 eV that N-doped ZnO thin film can function under visible light. Photocatalytic activity of prepared N-doped ZnO thin film was evaluated by the degradation of heavy metals in dairy milk. Duration of N-doped ZnO thin film degradation was found to vary from 0, 60, and 120 to 180 minutes. Heavy metal content in dairy milk is 0.5775 ppm. Addition of N-doped ZnO thin film to dairy milk reduced heavy metal content to 0.0053 ppm. In can then be inferred that heavy metal degradation using N-doped ZnO thin film is by as much as 89-99 %.

1. Introduction
Researchers are interested in the photocatalytic nature of semiconductors with promising technological applications [1]. Semiconductors are even more appealing with their superior properties, namely conductivity, magnetic and optical properties, high compatibility and sensitivity to chemical species [2]. One of the semiconductor photocatalysts is Zinc Oxide (ZnO) [3]. ZnO semiconductors have direct band gap which is useful in various applications such as photocatalysis and heavy metal degradation [4].

Zinc Oxide (ZnO) has a direct gap and width of 3.37 eV that it only works in UV light [5]. It is expected that ZnO can also work in visible light. As solar radiation is 45% visible light and 10% UV light, it is necessary to add cations (transition metals) and anions (carbon, sulphur, boron, and nitrogen) into semiconductor materials [6-7]. They are meant to improve photocatalytic activities of semiconductors.

Performance of ZnO in its application can be increased by adding metal to it. In this case, nitrogen (N) can be added to ZnO to increase its efficiency. N ion scanning acts as an acceptor in ZnO and can alter ZnO ions. Other than that, the addition of N ions can increase the absorption of light wavelengths. This is because the addition of N ions reduces energy gap in semiconductors [8-10].
Several methods for synthesizing N-doped ZnO have been developed. These include pyrolysis spray [11], pulsed laser deposition (PLD) [12], metal oxide chemical vapour deposition (MOCVD) [13], hydrothermal processes [14], wet chemical processes [15], reactive magnetron sputtering [16], high energy milling [17], pulsed laser deposition[18], and sol-gel [19,20]. The most widely used method is the sol-gel method because the material is easily prepared and it is of low cost. This research studies N-doped ZnO thin films with sol-gel method using a spray coating technique.

In its application, N-doped ZnO photocatalysts can be used to reduce heavy metal contamination. It is known that heavy metal contamination also affects food products such as milk. Heavy metal contamination in dairy milk involves Lead (Pb), Arsenic (As), Cadmium (Cd) and Mercury (Hg) which pose threats to human health upon consumption [21]. Earlier studies have shown that heavy metal contamination in milk exceeds the Indonesian National Standard level as it is detected to contain 0.53-1.31 ppm [22] and 0.1-1.4 ppm of Pb [23], which is way above the standard level of 0.02 ppm for Pb, 0.03 ppm for Hg, and 0.1 ppm for As [24]. Dairy farmers must ensure the safety of their produce. Therefore there is a need for a method to reduce heavy metal contamination and one of the solutions is by using N-doped ZnO photocatalysts.

2. Materials and methods

2.1. Materials

The materials used in this research were all chemicals in the reagent class and were used without further purification. The precursor was Zinc acetate dihydrate (Zn (COOCH₃), 2H₂O, Isopropanol ((CH₃)₂CHOH). The solvent and stabilizer were monoethanolamine (C₂H₇NO). Urea (CH₄N₂O) was used as source of nitrogen. Glass was sterilized using methanol (CH₃OH), acetone (C₃H₆O) and distilled water. Meanwhile, the N-doped ZnO was deposited on the glass.

2.2. Deposition of N-doped ZnO thin film

![Figure 1. Schematic diagram of N-doped ZnO thin film deposition.](image-url)
Deposition of N-doped ZnO thin film was performed by sol-gel method using spray coating technique. The schematic for the formation of deposition is shown in figure 1. The sol-gel method was started with dissolving Zinc acetate dehydrate, Zn (COOCH₃)₂.2H₂O in 2-propanol (CH₃CH (OH) CH₃) at 60° C to obtain a 0.3 M solution. The solution was stirred for 15 minutes. Then, monoethanolamine (MEA) was added dropped-wise into the solution while stirring for 15 minutes to obtain a clear solution of ZnO at 60° C. In case of making N-doped ZnO thin films and then nitrogen from urea (CH₄N₂O) was mixed into a clear solution Zinc acetate dehydrate to produce a weight ratio of ZnO-40% N. The solution was stirred for 30 minutes.

Glass substrate sterilization uses the Radio Corporation of America (RCA) method. This was conducted before deposition the N-doped ZnO solution on the glass substrate. Glass substrate was cleaned by acetone, and methanol for 10 min. Glass was placed in an ultrasonic cleaner because it was useful for washing dust and oil. Then, the glass was soaked in distilled water for 8 minutes and substrates were dried using a compressor gun. Before being deposited, the glass was heated at 450° C for 10 minutes. The N-doped ZnO solution which was successfully made was then sprayed onto the glass substrate for 1 hour at 450° C using spray coating technique. Furthermore, N-doped ZnO thin film was annealed at 450° C for 1 hour.

2.3. Degradation process
Experiments were carried out by comparing dairy milk without degradation of N doped ZnO thin films and milk with degradation of N-doped ZnO thin films. The schematic diagram of degradation process is shown in figure 2. N-doped ZnO thin films were activated in visible light. The degradation process was carried out on a laboratory scale. 200 ml of fresh milk was put into a cup and then illuminated by visible light.

**Figure 2.** Schematic diagram of degradation process.

Degradation efficiency of heavy metal in milk ($\eta$) was calculated using:

$$\eta = \frac{(C_0 - C)}{C_0} \times 100$$

Where $C_0$ is concentration and $C$ is degradation concentration by photocatalysis after t minutes.
2.4. Optical characterisations of prepared thin film

X-Ray Diffraction (XRD) analysis of the samples to determine structural characterization was carried out at room temperature with a diffractometer (Philips type 7000 diffractometer meter (40 kV, 30 mA) using nickel filters and copper radiation). Optical absorbance of N doped ZnO thin films was carried out using UV-Vis spectrophotometer (Shimadzu 1240 SA). FTIR (Fourier Transform Infra-Red) analysis of N doped ZnO was carried out by PerkinElmer Spectrum IR Version 10.6.1 to see the functional groups of N-doped ZnO thin films that is, showing the relationship of N and ZnO bonds in the sample.

3. Results and discussion

3.1. UV-visible spectrophotometer analysis

Figure 3. UV-Visible light absorption of the N-doped ZnO.

The UV-Vis (Visible Spectrophotometer) spectrophotometer analysis aimed to determine the optical properties of N-doped ZnO thin films (ZnO-40% N). Result were data in the form of a relationship between absorbance and transmission of light to materials in the absorption spectrum of wavelengths between 300-800 nm. Absorbance is the percentage of light intensity absorbed by a thin layer, while transmittance is the percentage of the intensity of light transmitted by a thin layer. Data from this sample uses transmittance, as shown in figure 3. Transmission in doped material (ZnO-40% N) shifts from the material value without doping transmittance (ZnO). ZnO shows UV absorption band at 310 nm. The presence of N dopant on a photocatalyst may affect optical properties of ZnO. The absorption peak shifts towards the visible light spectrum.

Figure 4. Bandgap of N-doped ZnO thin film.
Absorption of the ZnO region is extended to the visible light region. This is caused by the resonance absorption of plasmon N surface nanoparticles. Absorption peak of N-doped ZnO thin films at around 380 nm was observed, which must be associated with the absorption characteristics of N nanoparticles [25]. This shift shows the movement of electrons from the level of metal N to ZnO nanoparticles. Graphs generated from UV-Vis testing can be used to find thin layer energy gap values.

It can be seen in the graph of UV-Vis in figure 3 that the peak is formed in the range of 366 nm. If plotting is done using the tauch plot method shown in figure 4, N-doped ZnO band gap of 3.2 eV is obtained, which can work in visible light.

3.2. XRD (X-Ray Diffractogram) analysis

XRD pattern of N-doped ZnO thin films have been obtained from the approved sol-gel method, as shown in figure 1. Results of XRD pattern for N-doped ZnO thin film were confirmed using JCPDS 36-1451 for the analysis of ZnO and JCDPS No. 23-1294 for the analysis of N. In the thin films, ZnO and N were found at all peaks. Bare diffraction peaks were found to be (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 0 0), and (2 0 0). Other researchers suggest that ZnO peak patterns are similar to all samples. They conclude that the addition of both nitrogen and various syntheses did not alter the crystal structure of ZnO [20].

In a study reported by another group, it was also explained that thin films show evidence of polycrystalline structure that is hexagonal [26,27]. On this occasion, diffraction peaks (1 0 0) and (0 0 2) will be analysed for samples. The catalyst is of single-phase because no additional peaks were observed. It is observed that with N doping, the peak is expanded and the intensity is lowered. This is most likely due to a decrease in crystallinity as a result of crystal growth inhibition by urea [20] or because of O replacement with N [28]. The presence of these peaks shows that N-doped ZnO thin films have good crystal structure [29].

Figure 5. XRD spectrum of N-doped ZnO thin film.

In figure 5, 2 main peaks showing the structure of N-doped ZnO crystal was analysed and it is in line with results from an earlier study [2]. The first peak is located at 31.879 of 2 theta, which is the characteristics Wurtzite hexagonal structure of ZnO (JCDPS file No. 36-1451). The second peak is located at 33.941 of 2 theta, which is the characteristic hexagonal structure of N (JCDPS file No. 23-1294).
3.3. **FTIR (Fourier Transform Infrared) analysis**

FTIR analysis aims to find the functional groups produced. In this research, FTIR analysis was performed on N-doped ZnO thin film synthesized by sol-gel method using zinc acetate dehydration and nitrogen.

Resulting curve from FTIR analysis on N-doped ZnO film can is given in figure 6. The peak at 892.62 cm\(^{-1}\) shows ZnO [30]. In general, all metals and metal oxides have peaks at a voltage of 400-800 cm\(^{-1}\). The peak at 1541 cm\(^{-1}\) shows N = N (nitrogen) [31]. The vibration at 3409.37 cm\(^{-1}\) shows the O-H voltage vibration [18]. Therefore, it can be concluded that N-doped ZnO thin films was successfully made as proven in the presence of ZnO and N functional groups.

3.4. **Degradation of heavy metal in dairy milk using N-doped ZnO thin film**

Table 1 show that the use of N-doped ZnO thin films can reduce heavy metal content in dairy milk. Decrease in the content of Pb, Hg and As in dairy milk is shown here.

**Table 1.** Effects of addition of N-doped ZnO thin films on dairy milk during the degradation process.

| Test  | SNI (2011) | Before Storage | After Storage | Unit | Method |
|-------|------------|----------------|---------------|------|--------|
| Pb    | 0.02       | 0.7            | 0.01          | ppm  |        |
| Hg    | 0.03       | 0.2            | 0.02          | ppm  | AAS    |
| As    | 0.1        | 0.5            | 0.1           | ppm  |        |

Table 1 shows test results for the heavy metal content of dairy milk using AAS method. It can be seen that dairy milk contents before storage are lead (Pb) 0.7 ppm, mercury (Hg) 0.2 ppm and arsenic (As) 0.5 ppm, while after storage the contents are Pb 0.01 ppm, Hg 0.02 ppm and As 0.1 ppm, respectively. N-doped ZnO thin films reduce the content of heavy metals Pb, Hg, As in dairy milk, hence, the test was successful. These results indicate heavy metal contents are now in agreement with SNI (Indonesian National Standard) requirements. According to SNI, fresh milk should only contain Pb of 0.02 ppm, As of 0.1 ppm and Hg of 0.03 ppm, respectively.
Table 2. Effect of varied addition time of N-doped ZnO thin films on the degradation of Pb in dairy milk.

| Time (minutes) | Pb content (ppm) | Decrease Percentage (%) | SNI (2011) |
|---------------|------------------|--------------------------|------------|
| 0             | 0.5775           | 0                        | 0.02       |
| 60            | 0.0273           | 91.81                    | 0.02       |
| 120           | 0.0113           | 96.61                    | 0.02       |
| 180           | 0.0053           | 99.08                    | 0.02       |

It can be seen in Table 2 that longer addition time of N-doped ZnO thin films on Pb degradation in dairy milk shows significant results. Pb degradation at minute 0 is 0.5775 ppm. Meanwhile, Pb degradation at minute 60 is 91.81%, that is 0.0273 ppm. Pb degradation at 120 minutes is 0.0113 ppm with a reduction percentage of 96.61%. The best results were obtained at minute 180 with 0.0053 ppm, at a reduction percentage of 99.08%. This means that Pb degradation was successful. Pb level is now in agreement with SNI requirements. According to SNI, fresh milk should only contain Pb of 0.02 ppm.

3.5. Analysis of dairy milk quality

Photocatalytic activity in the degradation process is shown in Tables 1 and 2. Data there show reduction in metal (Pb, Hg, and As) content due to photocatalytic activity. Photocatalytic process occurs when N-doped ZnO materials are irradiated by light so that the energy is greater than the ZnO gap energy. A schematic diagram of the mechanism of heavy metal degradation reactions on the surface of N-doped ZnO nanoparticles is shown in Figure 7.

![Figure 7](image_url)

**Figure 7.** Schematic diagram of the mechanism of heavy metal degradation reactions on the surface of N-doped ZnO nanoparticles.

The working principle of a photocatalyst is the activation of semiconductors by the energy of photons that produce electron-hole pairs (e⁻ / h⁺) followed by the formation of radical ions. Electrons and holes then react with dissolved oxygen and OH superoxide (O₂⁻) and hydroxyl radicals (OH * ) [32]. Several recent studies have proven that ZnO has high efficiency because of its ability to produce H₂O₂ more efficiently than TiO₂. [33].

ZnO is a p-type semiconductor material. P-type semiconductors have more whole concentrations than n-type semiconductors. Thus, ZnO holes are denser and hydroxyl formation is more radical (OH*). Viewed from the number of valence electrons, the OH reactivity is higher than O₂*-. This explains that...
OH* lacks one electron while O$_2^*$ has one extra electron and this makes OH* more likely to reach equilibrium [34]. The addition of N to ZnO results in better load separation. The presence of N ions increases photocatalyst activity because it traps photoelectrons that react with the surface of absorbed oxygen molecules [35]. Radical hydroxyl that has been produced reacts with organic molecules and breaks down organic compounds into other intermediate compounds which in turn, undergo further reactions. Excited electrons react with oxygen to form superoxide anion species. Superoxide anions react with compounds that break down organic molecules. Interactions between dairy milk and compounds produced during degradation process degrade heavy metal content in dairy milk.

4. Conclusion
Photocatalytic degradation of heavy metals (Pb, Hg and As) in dairy milk by N-doped ZnO thin film using spray coating technique was successfully carried out. A systematic study of the effect of N-doped ZnO content on the optical properties of thin films, the morphological of thin films, functional groups in thin films, time variations in the duration of Pb heavy metal degradation and photocatalytic activity of thin films were successfully carried out. In principle, ZnO can be activated in UV light without doping. The band gap of N-doped ZnO thin film becomes small so that it can be activated using visible light. Addition of N to ZnO also increases photocatalyst activity in degrading heavy metals (Pb, Hg, As) content in fresh dairy milk. After the addition of N-doped ZnO thin film to dairy milk, there is a decrease in the content of heavy metals by 0.0053 ppm, which is an 89-99 % reduction. These experimental results of Pb heavy metal degradation in dairy milk are satisfactory they are in agreement with SNI requirements.

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References
[1] Serpone N and Emeline A V 2012 Semiconductor photocatalysis past, present and future outlook J. Phys. Chem. Lett. 3(2012) 673-677
[2] Gionco C, Debora F, Calza P and Paganini M C 2016 Synthesis, Characterization, and Photocatalytic Tests of N-Doped Zinc Oxide: A New Interesting Photocatalyst Journal of Nanomaterials 2016 1-7
[3] Sutanto H, Nurhasanah I and Hidayanto E 2015 Deposition of Ag$_2$~6mol% -doped ZnO photocatalyst thin films by thermal spray coating method for E. coli bacteria degradation Materials Science Forum 827 3–6
[4] Poongodi G, Kumar R M and Jayavel R 2015 Structural, optical and visible light photocatalytic properties of nanocrystalline Nd doped ZnO thin films prepared by spin coating method Ceramics International 41(3) 4169–4175
[5] Lamba R, Umar A, Mehta S K and Kansal S K 2015 Well-crystalline porous ZnO-SnO$_2$ nanosheets: an effective visible-light driven photocatalyst and highly smart sensor material Talanta 131(2015) 490-498
[6] Anandan S, Ohashi N and Miyauchi M 2010 ZnO-based visible-light photocatalyst: band-gap engineering and multi-electron reduction by co-catalyst Applied Catalysis B: Environmental 100(3-4) 502–509
[7] Nair M G, Nirmala M, Rekha K and Anukalani A 2011 Structural, optical, photocatalytic and antibacterial activity of ZnO and Co-doped ZnO nanoparticles Materials Letters 65(12) 1797–1800
[8] Bian H Q, Ma S Y, Zhang Z M, Gao J M and Zhu H B 2014 Microstructure and Raman scattering of Ag-doping ZnO films deposited on buffer layers Journal of Crystal Growth 394 132–136
[9] Zhang Y, Zhang Z, Lin B, Fu Z and Xu J 2005 Effects of Ag doping on the photoluminescence of ZnO films grown on Si substrates The Journal of Physical Chemistry B 109(41) 19200–19203

[10] Fan J and Freer R 1995 The roles played by Ag and Al dopants in controlling the electrical properties of ZnO varistors Journal of Applied Physics 77(9) 4795–4800

[11] Zhao J L, Li X M, Bian J M, Yu W D and Zhang C Y 2005 Growth of nitrogen-doped p-type ZnO films by spray pyrolysis and their electrical and optical properties J. Cryst. Growth 280(2005) 495–501

[12] Li Q, Wang Y, Liu J, Kong W and Ye B 2014 Structural and magnetic properties in Mn-doped ZnO films prepared by pulsed-laser deposition Applied Surface Science 289 42–46

[13] Biethan J P, Sirkeli V P, Considine L, Nedeoglo D D, Pavlidis D and Hartnagel H L 2012 Photoluminescence study of ZnO nanostructures grown on silicon by MOCVD Materials Science and Engineering: B 177(8) 594-599

[14] Gautam U K, Panchakarla L S, Dierre B, Fang X, Bando Y, Sekiguchi T ... and Rao C N R 2009 Solvothermal Synthesis, Cathodoluminescence, and Field-Emission Properties of Pure and N-Doped ZnO Nanobullets Advanced Functional Materials 19(1) 131-140

[15] Bhirud A P, Sathaye S D, Waichal R P, Nikam L K and Kale B B 2012 An eco-friendly, highly stable and efficient nanostructured p-type N-doped ZnO photocatalyst for environmentally benign solar hydrogen production Green Chemistry 14(10) 2790-2798

[16] Nakano Y, Morikawa T, Ohwaki T and Taga Y 2005 Deep-level characterization of N-doped ZnO films prepared by reactive magnetron sputtering Applied Physics Letters 87(23) 232104

[17] Lu J, Zhang Q, Wang J, Saito F and Uchida M 2006 Synthesis of N-Doped ZnO by grinding and subsequent heating ZnO-urea mixture Powder technology 162(1) 33-37

[18] Duclère J R, Novotny M, Meaney A, O’Haire R, McGlynn E, Henry M O and Mosnier J P 2005 Properties of Li-, P-and N-doped ZnO thin films prepared by pulsed laser deposition Superlattices and Microstructures 38(4-6) 397-405

[19] Sutanto H, Nurhasanah I and Hadiyanto H 2014 Effect of Mn concentration on magnetic and structural properties of GaN: Mn deposited on silicon substrate using chemical solution deposition method Revista Romana De Materiale-Romanian Journal Of Materials 44(3) 298-303

[20] Qin H, Li W, Xia Y and He T 2011 Photocatalytic activity of heterostructures based on ZnO and N-doped ZnO ACS applied materials & interfaces 3(8) 3152-3156

[21] Brown G E and Parks G A 2001 Sorption of trace elements on mineral surfaces: Modern perspectives from spectroscopic studies, and comments on sorption in the marine environment Int. Geol. Rev. 43 963–1073

[22] Salundik S, Suryahadi S, Mansjoer S S, Sopandie D and Ridwan W 2012 Cemaran timbal (Pb) dan arsen (As) pada susu sapi perah yang diberi pakan limbah organik pasar di peternakan sapi perah Kebon Pedes Bogor Jurnal Peternakan Indonesia (Indonesian Journal of Animal Science) 14(1) 308-318

[23] Harlia E, Rahmah K N and Suryanto D 2018 Food safety of milk and dairy product of dairy cattle from heavy metal contamination IOP Conference Series: Earth and Environmental Science 102(1) 012050

[24] National Standardization Agency 2011 Indonesian National Standard (SNI): SNI Number 3141.1: 2011. Fresh Milk - Part 1: Cow (Jakarta: National Standardization Council)

[25] Wang T, Jiao Z, Chen T, Li Y, Ren W, Lin S, ... and Bi Y 2013 Vertically aligned ZnO nanowire arrays tip-grafted with silver nanoparticles for photoelectrochemical applications Nanoscale, 5(16) 7552-7557

[26] File P D 1967 Joint committee on powder diffraction standards (Philadelphia, Pa: ASTM) 9-185

[27] Chen X and Mao S S 2007 Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications Chemical Reviews 207(7) 2891–2959
[28] Patil A B, Patil K R and Pardeshi S K 2011 Enhancement of oxygen vacancies and solar photocatalytic activity of zinc oxide by incorporation of nonmetal *J. Solid State Chem.* 184(2011) 3273–3279

[29] Saboor A, Shah S M and Hussain H 2019 Band gap tuning and applications of ZnO nanorods in hybrid solar cell: Ag-doped verses Nd-doped ZnO nanorods *Materials Science in Semiconductor Processing* 93 215-225

[30] Ningsih S K W and Khair M 2015 *Sintesis dan Karakterisasi Nanopartikel ZnO Melalui Proses Sol-Gel untuk Bahan Solar-Cell* (Padang: Universitas Negeri Padang)

[31] Chang M C, Shu H Y, Tseng T H and Hsu H W 2013 Supported zinc oxide photocatalyst for decolorization and mineralization of orange G dye wastewater under UV365 irradiation *International Journal of Photoenergy* 2013 1-12

[32] Robertson P K, Robertson J M and Bahnemann D W 2012 Removal of microorganisms and their chemical metabolites from water using semiconductor photocatalysis *Journal of hazardous materials* 211 161-171

[33] Bizarro M 2010 High photocatalytic activity of ZnO and ZnO: Al nanostructured films deposited by spray pyrolysis *Applied Catalysis B: Environmental* 97(1-2) 198-203

[34] Habibi M H and Khaledi Sardashti M 2008 Preparation and proposed mechanism of ZnO Nanostructure Thin Film on Glass with Highest c-axis Orientation *International Journal of Nanoscience and Nanotechnology* 4(1) 13-16

[35] Xu Y C and You H 2014 TiO2 modified with Ag nanoparticles synthesized via ultrasonic atomization-UV reduction and the use of kinetic models to determine the acetic acid photocatalytic degradation *Applied Surface Science* 321 481-487