

Electrospun Cellulose Acetate/Maleic Acid Functionalized Gold Nanoparticles as Pb(II) Ions Colorimeter Sensor Strip

Pimolpun Niamlang^{1*}, Chularat Iamsamai¹, Piyanut Muangtong¹,
Piyachat Chuysinuan²

¹Department of Materials Engineering, Faculty of Engineering, Rajamangala University of Technology Rattanakosin, Phutthamonthon, Nakhonpathom 73170, Thailand

²Laboratory of Organic Synthesis, Chulabhorn Research Institute, Bangkok 10210, Thailand

*Corresponding author e-mail: pimolpun.kam@rmutr.ac.th

Received: 10 February 2024 / Revised: 14 May 2024 / Accepted: 28 June 2024

Abstract

This study investigates the synthesis of gold nanoparticles and surface modifications to enable their utilization as a colorimetric sensor strip on electrospun nanofibrous. Additionally, it utilizes cellulose acetate electrospun fiber preparations as substrates for loading the gold nanoparticles. In order to produce gold nanoparticles, citrate reduction was employed, followed by modification with maleic acid (MA-GNPs). MA-GNPs were significantly more selective for Pb²⁺ than for other ions (Co²⁺, Cu²⁺, Hg²⁺, Ni⁺), according to the results. Following the introduction of Pb²⁺, the solutions exhibited a color change from red to blue or purple, which was attributed to the aggregation of nanoparticles, as determined by UV-Vis spectrometry. An optical band indicative of GNPs and MA-GNPs was detected at an estimated wavelength of 520 nm. Approximately 600 nanometers after the addition of Pb²⁺, the intensity of the solution progressively decreased to 520 nanometers, and a new band emerged. To fabricate cellulose acetate nanofibrous via electrospinning, the impact of solvent ratios, polymer concentrations, and process conditions were investigated. The ideal parameters for the fabrication of the substrate were as follows: 15% w/w polymer solution, 15 kV electrospinning voltage, 15 cm needle-to-collector distance, and 48 hours of collecting time. In order to examine the color change of the prepared strip, it is observed that the strip transforms from red to blue upon exposure to Pb²⁺ ions of varying concentrations, just as it does in solution form. An examination of water samples indicated that the strip remained colorless when tested with DI water. However, testing with wastewater sourced from a battery facility identified a transformation of the strip from red to purplish blue. This is equivalent to an estimated lead concentration of 40 parts per million. The outcomes showcased the capacity of the discolored strips to identify the preliminary concentration of lead ions, suggesting potential for future advancements in this area.

Keywords: Gold nanoparticle, Lead detection, Electrospinning process, Colorimetric sensor, Sensor strip

1. Introduction

The pollution of harmful substances in soil and water is currently a serious topic being addressed by a number of parties. This issue has a profound impact on the environment, ecosystems, public health, and human livelihoods. Rapid industrialization, technological advancement, and economic growth have resulted in the emission of pollutants beyond permissible limits, resulting in major and difficult environmental challenges. One of the consequences is heavy metal leakage and poisoning of water supplies (Abdullah, Yusof, Lau, Jaafar, & Ismail, 2019; Feng et al., 2022).

Heavy metals are elements with a specific gravity greater than four, and they are primarily members of the transition metals group. They accumulate in soil and water because they are persistent and incapable of breaking down naturally (Feng et al., 2022). Heavy metals are crucial in numerous industries, including plastics, PVC, paint, and agricultural products such as fertilizer and insecticides (Chen & Wang, 2004; Fewtrell, Kaufmann, & Prüss-Üstün, 2003; Han, Zou, Zhang, Shi, & Yang, 2006). In everyday living, people are at danger of swallowing heavy metals through food or water that contains these compounds. Communities living near factories may

contribute to inappropriate waste disposal methods, resulting in soil and water contamination. This contamination has a negative influence on aquatic life, compromising the delicate balance of ecosystems required to maintain life. The government recognizes the importance of this issue and has put in place guidelines for managing industrial wastewater outflow. For example, in compliance with the Factory Act of 1992, the Ministry of Industry issued regulations in 2017 to regulate the emission of heavy metals from industries. The laws establish allowable limits for elements like zinc and copper in wastewater (World Health Organization, 2004).

Traditional techniques such as Atomic Absorption Spectroscopy (AAS) and Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS) have been used to monitor heavy metal ions (Ghaedi, Ahmadi, & Shokrollahi, 2007; Milne, Landing, Bizimis, & Morton, 2010). These approaches have limitations, such as high costs, complex operations, and high professional requirements. In comparison, the colorimetric method for heavy metal ions has gained growing attention due to its many advantages, particularly with regard to prompt and on-site detection. Specifically, its portability allows for field analysis, rapid detection using the naked eye without complex instruments, and ease of use for non-experts, suggesting significant potential for future applications.

A colorimetric sensor system for environmental and medical applications has been developed in response to these concerns. The sensor device, which employs gold nanoparticles, provides an affordable and user-friendly alternative to standard approaches. Furthermore, the use of nanomaterials, such as nanofibers and nanowebs electrospun (Huang, Zhang, Kotaki, & Ramakrishna, 2003) improves the sensitivity and biocompatibility of the sensing platform (Chansuwan, 2022; Hammami, Alabdallah, Al jomaa, & Kamoun, 2021; Ratnarathorn, Chailapakul, & Dungchai, 2015; Sartore, Barbaglio, Borgese, & Bontempi, 2011).

This study aims to investigate the properties of maleic acid-modified gold nanoparticles/electrospun cellulose acetate nanofiber mats as a sensor platform for identifying color shifts related to concentrations of heavy metal ions.

2. Materials and Methods

2.1 Materials

HAuCl₄ was purchased from Alfa Aesar, United States. Tri-sodium citrate was purchased from Ajax Finechem, Auckland. Maleic acid from TCI, Japan. Cellulose acetate, N, N-Dimethylacetamide (DMAc), and acetone were purchased from Sigma-Aldrich. All metal nitrate salts were AR grade from QR&C®, New Zealand.

2.2 Preparation of electrospun cellulose acetate nanofiber mats

As a supporting platform or test strips, cellulose acetate was formed into nanofiber mats. A 15% w/v cellulose acetate solution was made by dissolving it in a 2:1 solvent mixture of acetone and N, N-Dimethylacetamide (DMAc) (Zhang et al., 2019). The solution was stirred for 10 hours at room temperature using a magnetic stir bar until the solution became clear. The obtained solution was then electrospun into nanofibers using an electrospinning device with the electric voltage adjusted sequentially to 10, 12.5, and 15 kV. The needle tip to collector distance was 20 cm, and the solution was allowed to spin for 15 minutes. SEM (Scanning Electron Microscopy) was used to evaluate the resultant nanofibers for morphological properties, and Image J was used to measure size. The nanofiber mats were then formed for 2 hours and their thickness was measured with a micrometer. Finally, the nanofiber mats were dried in an air oven at room temperature (25°C) to eliminate any residual solvent.

2.3 Preparation of Maleic Acid/Gold Nanoparticles (MA-GNPs)

The preparation of gold nanoparticles using the method developed by Nalin Ratnarathorn and colleagues (Ratnarathorn et al., 2015) involves a modified procedure, which can be summarized as follows: A volume of 100 ml of tetrachloroauric acid solution with a concentration of 0.01% w/v is placed in a 250-ml amber glass bottle. The solution is then heated until boiling. Subsequently, 3.5 ml of sodium citrate solution with a concentration of 1% w/v is added rapidly, and the mixture is vigorously stirred with a stirrer bar for 15 minutes. Continuous stirring without additional heating is maintained for another 30 minutes. The solution is then allowed to cool to room temperature and stored in a refrigerator at 4°C. The light absorption characteristics are analyzed using a UV-Vis spectrophotometer.

2.4 Measurement of heavy metal ions

2.4.1 Measurement using MA-GNPs solution

A 1000 ppm solution of heavy metal ions, including Co^{2+} , Cu^{2+} , Hg^{2+} , Ni^{+} , and Pb^{2+} ions, was prepared. This solution was then diluted to quantities ranging from 10 to 100 ppm. To evaluate the detection capability of heavy metal ions, the diluted heavy metal ion solution was dropped into the MA-GNPs solution in quantities of 5, 10, 20, 30, 40, and 50 μl .

2.4.2 Measurement using MA-GNPs on cellulose acetate nanofiber mats

The cellulose acetate nanofiber mats were impregnated with MA-GNPs by dropping the MA-GNPs solution onto the nanofiber mats and allowing them to dry at room temperature. The detection of heavy metal ions was then tested by dropping 10-100 ppm heavy metal ion solutions onto the MA-GNPs-impregnated nanofiber mats. The results were recorded using a high-resolution camera for color comparison.

3. Results and Discussion

3.1 The condition of electrospinning

The size of electrospun cellulose acetate fibers was measured using different electrostatic voltages (10, 15, and 20 kV). The following parameters were maintained: a cellulose acetate concentration of 15% w/v in a solvent mixture of acetone and N, N-dimethylacetamide (DMAC) in a 2:1 ratio, a needle tip-to-collector distance of 15 cm, and a spinning period of 2 hours. Subsequently, the fiber diameters were examined using scanning electron microscopy (SEM), with the results shown in Figure 1.

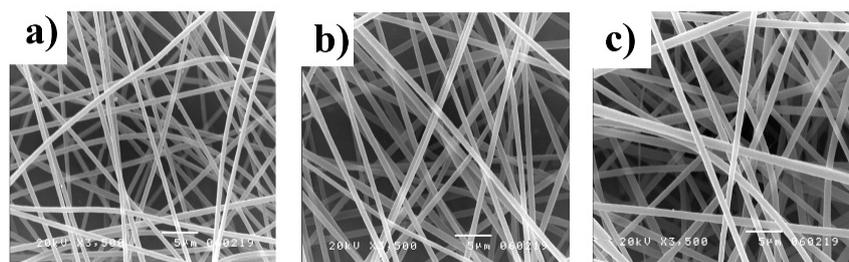


Figure 1. SEM images of cellulose acetate fiber mat using electrospinning at different electric potential: (a) 10 kV, (b) 15 kV, and (c) 20 kV, respectively.

The optimal conditions for cellulose acetate fiber mat production are unquestionably 15 kV electrospinning voltage. The observed fiber diameters from SEM images reveal average diameters of 0.666, 0.620 and 0.795 nm and average variations of 0.0814, 0.0468, and 0.1237 for electrospinning voltages of 10, 15, and 20 kV, respectively. Additionally, 15 kV fibers showed the lowest average deviation, indicating more consistent and stable fiber diameters than 10 and 20 kV fibers. This means that a 15 kV electrospinning voltage results in more uniform and stable fiber diameters, showing its suitability for the electrospinning process, which will be studied further.

3.2 Concentration of maleic acid-modified gold (MA-GNP)

A gold nanoparticle solution with a volume of 0.4 milliliters was used to test the synthesis of gold nanoparticles (GNPs) treated with maleic acid. In order to modify the surface, an acid-modifying solution was mixed in a volume of 0.20 milliliters at various concentrations (5, 10, 15, and 20 millimolar). Figure 2(a) shows how the results were analyzed with a UV-Vis Spectrophotometer (Hammami et al., 2021).

The greatest absorption value of nanoparticles made by the citrate reduction technique was observed at 520 nm in wavelength. When utilizing acid concentrations of 10 mM or above, the absorption at 520 nm started to decrease after the surface was modified. This phenomenon can be attributed to the hydrogen bonding that occurs between the particles (Ding et al., 2010). Figure 2(b), which shows the relationship between the absorbance value at 520 nm and the concentration of maleic acid-modifying solution, illustrates this result.

These MA-GNP were selected for further heavy metal ion detection testing since the results also show that a 10 mM of maleic acid concentration is optimum for surface modification.

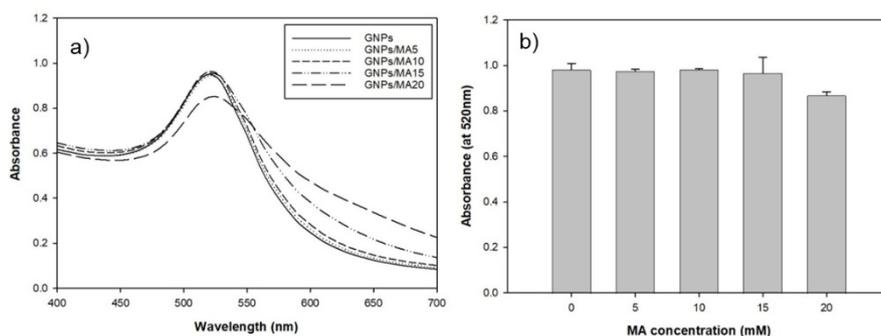


Figure 2. (a) Absorption wavelength range of 400-700 nm of gold nanoparticle with concentration of maleic acid solution from 0 - 20 mM (b) Relationship between acid concentration affecting the light absorption of gold nanoparticles at 520 nm.

4.3 Detection of heavy metal ions

4.3.1 Preliminary detection using MA-GNPs solution

The preliminary heavy metal ion detection tests involved five types of metal ions: Co^{2+} , Cu^{2+} , Hg^{2+} , Ni^{+} , and Pb^{2+} . A volume of 0.4 ml of metal ion solution with a concentration of 50 ppm was added to the MA-GNPs solution with a volume of 0.6 ml. After 15 minutes, the spectral analysis using UV- VIS Spectrophotometer revealed a clear change in the absorption spectra, as depicted in Figure 3.

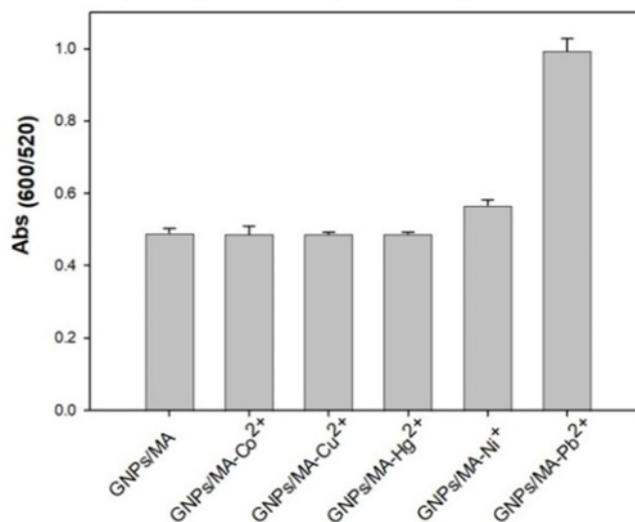


Figure 3. Detection of Co^{2+} , Cu^{2+} , Hg^{2+} , Ni^{+} , and Pb^{2+} ions using MA-GNPs with an acid concentration of 10 mM.

The absorption ratio ($A_{600/520}$) demonstrated distinct changes after 15 minutes when adding ions such as Co^{2+} , Cu^{2+} , Hg^{2+} , and Ni^{+} . This indicates the high specificity of the detection method for lead ions. It was observed that the absorption ratio increased when the concentration of ions increased. The results suggest that MA-GNPs can effectively detect lead ions with high sensitivity and selectivity.

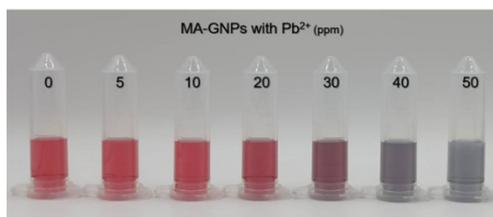


Figure 4. Color change of MA-GNP particles after adding Pb^{2+} ions of different concentrations.

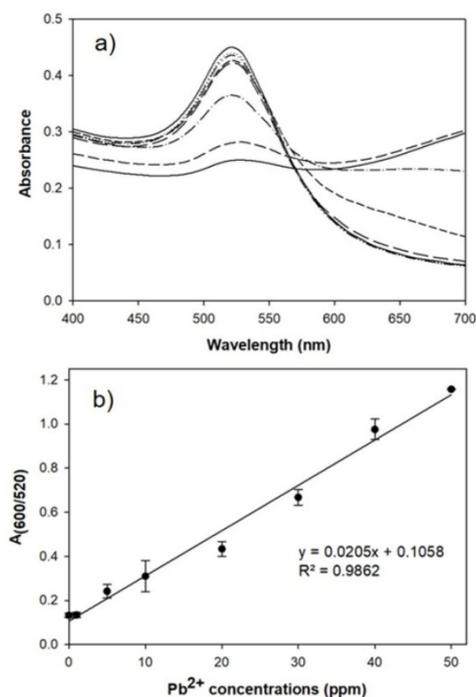


Figure 5. (a) Absorption Spectrums by MA-GNP after the addition of varying concentrations of Pb(II) ions. (b) Linear correlation between the absorbance ratio A600/520 and the concentration of Pb(II) ions in the range of 0-50 ppm.

The investigation of MA-GNPs nanoparticles for detecting lead ions at varied concentrations revealed distinct color intensity levels and change in the absorption spectra. As the concentration of lead ions increases, the color response of the solution shifts from red to blue, as can be observed in Figure 4. The graph indicates the changes in absorption of light values caused by varying lead ion concentrations.

Figure 5(a) indicates the shift in light absorption at 520 nanometers, which reduces, and at 600 nanometers, which increases. This suggests that the ability of MA-GNPs to aggerating lead ions corresponds to their concentration (Li et al., 2014). In addition, Figure 5(b) shows a linear relationship between the absorption ratio (A600/520) and the concentration of lead ions ranging from 10 to 100 ppm ($R^2 = 0.9862$).

4.3.2 Detection using cellulose acetate fiber mats loaded with MA-GNPs

Lead ions were also detected using cellulose acetate fiber mats coated with MA-GNPs. The mats were made by dropping a 100- μ l solution of MA-GNPs into 10x10 mm cellulose acetate fiber mats and air-drying them. Color changes were detected after the electrospun fiber mats were subjected to Pb(II) ion solutions of different concentrations (0, 10, 20, 30, 40, and 50 ppm). The results are shown in Figure 6.

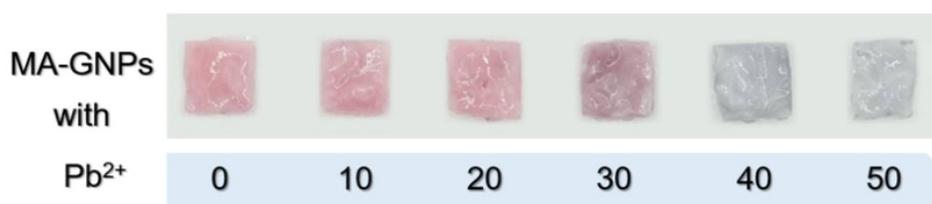


Figure 6. Color change of cellulose acetate fiber mats loaded with MA-GNPs when exposed to citrate ion solutions of different concentrations (0, 10, 20, 30, 40, and 50 ppm).

The fast detection of lead ions by these membranes was observed by the naked eyes and digital camera. The images showed MA-GNPs/cellulose acetate fiber mats with incubated at 0, 10, 20, 30, 40, and 50 ppm. These results confirmed that the color changes from red to purple-blue in cellulose acetate fiber mats loaded with MA-GNPs were the result of the interaction between Pb^{2+} and MA-GNPs in nanofibers.

4.3.3 Detection from sample water

Pb(II) ions were detected using cellulose acetate fiber mats loaded with MA-GNPs in two types of water samples: DI and wastewater from a battery manufacturing company. A 100-micro-liter MA-GNPs solution was dropped onto 10x10 mm cellulose acetate fiber mats and air-dried. The fiber mats were then exposed to the water samples and color changes were noticed. The outcomes are depicted in Figure 7.

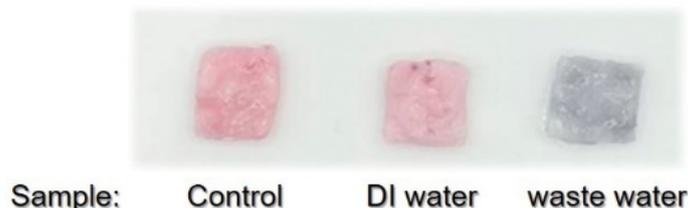


Figure 7. exhibits the color change of cellulose acetate fiber mats loaded with MA-GNPs after exposure to various water samples.

The fiber mats changed color from red to purple-blue when exposed to wastewater from the battery manufacturing company, according to the test results. According to the concentration analysis, this color shift was connected with a Pb(II) ions concentration of around 40 ppm. These findings show the new test strips' potential for preliminary detection of citrate ions and suggest further development for broader applications.

4. Conclusions

In summary, electrospun tailored cellulose acetate fiber mats were successfully loaded with selectively manufactured and surface-modified gold nanoparticles (MA-GNPs) of approximately 20 nm. These MA-GNPs changed color from red to purple when exposed to lead ion concentrations ranging from 0 to 100 ppm. The color shift correlated with lead ion concentration in a proportional manner, with an absorbance ratio (A_{600}/A_{520}) demonstrating a linear relationship in the 10 to 100 ppm range ($R^2 = 0.9862$). Furthermore, when exposed to lead ion-containing wastewater, these fiber mats had a similar color-changing response, demonstrating their use as preliminary lead ion detection tools in environmental monitoring applications. This points to intriguing future directions for the development and application of these color-changing strips in a variety of scenarios.

Acknowledgements

Authors wish to express their gratitude to National Research Council of Thailand (NRCT) for their financial support. We appreciate the ongoing collaboration with the Research and Development Institute at Rajamangala University of Technology Rattanakosin, the Organic Chemistry Synthesis Laboratory at Chulabhorn Research Institute, and the Department of Materials Engineering at Rajamangala University of Technology Rattanakosin. Their collective support, resources, and expertise have been instrumental in the success of our research.

ORCID

Pimolpun Niamlang
<https://orcid.org/0000-0003-1680-5316>

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