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20th
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NANO THAILAND 2023

The 8th Thailand International
Nanotechnology Conference

**"Nanotechnology for
Sustainable World"**

e-Proceeding

November 29- December 1, 2023
Dusit Thani Pattaya Hotel,
Chon Buri, Thailand

Sponsor



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The 8th International Conference on Nanotechnology – NanoThailand 2023
November 29 – December 1, 2023
Dusit Thani Pattaya, Chonburi, Thailand

e-Proceeding

NANOTHAILAND2023

The 8th Thailand International
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Welcome Message

From the Nanotechnology Association of Thailand and National Nanotechnology Center (NANOTEC)



Dr. Wannee Chinsirikul

Executive Director of the National Nanotechnology Center (NANOTEC) and President of the Nanotechnology Association of Thailand

On behalf of the Nanotechnology Association of Thailand, it is my great pleasure and privilege to extend a warm invitation to you all for participating the 8th Thailand International Nanotechnology Conference (NanoThailand 2023), which will be held during 29 November – 1 December 2023 at Pattaya, Chonburi, Thailand. I would like to take this opportunity to express my sincere appreciation to Vidyasirimedhi Institute of Science and Technology (VISTEC), National Nanotechnology Center (NANOTEC) and the Nanotechnology Association of Thailand to organize this conference.

The theme of the conference is “Nanotechnology for Sustainable World”. The objectives are to apply nanoscience and nanotechnology for a better life and well-being to create a platform for knowledge exchange to further advance technological areas, and to exhibit the latest innovations to the industries. At present, we are collaborating in areas such as e-science, renewable energy and the development of novel drugs to combat a range of infectious diseases. Therefore, Science, Technology, Innovation and technology know-how cooperation among peers are very important. NanoThailand 2023 will provide a platform for experienced researchers in nanotechnology and practitioners from both academics, as well as industry to meet and share cutting-edge development in the field. In order to meet the objectives of the conference, the world renowned speakers, and researchers are invited to present the advancement of nanoscience and to update trend of the World’s nanotechnology of their expertise.

I would like to welcome all participants, and to our overseas friends, please enjoy the breath and depth of Science and Technology at the upcoming NanoThailand 2023 (29 November – 1 December 2023) in the vibrant east coastal city of Thailand where you could take times to also absorb many attractive sites there is to offer in Pattaya.

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Welcome Message

Form Vidyasirimedhi Institute of Science and Technology (VISTEC)



Professor Dr. Pimchai Chaiyen

President of Vidyasirimedhi Institute of Science and Technology (VISTEC)

On behalf of Vidyasirimedhi Institute of Science and Technology (VISTEC), it is my great pleasure to welcome you all to the 8th Thailand International Nanotechnology Conference (NanoThailand 2023), being held between 29 November – 1 December 2023 at Dusit Thani Hotel, Pattaya, Thailand. VISTEC is proud to be a co-host of this conference.

The conference's theme is “Nanotechnology for Sustainable World” and its objectives are to apply nanotechnology in various fields to contribute to sustainable development. The conference will create a platform for technological knowledge exchange, and to share the latest progress in research and innovations towards a sustainable world. We are expecting around 350 participants from more than 20 countries to attend NanoThailand 2023. The conference features 13 sessions with 2 plenary lectures, 97 keynote and invited talks, 97 oral presentations and 82 posters covering all fields of nanotechnology.

On the scientific side, VISTEC members are contributing extensively to this conference by hosting, chairing, co-chairing, and presenting in all the sessions. Together with our co-host NANOTEC, we aim to showcase advanced and innovative nanoscience and nanotechnology research conducted in Thailand. Our members are hosting and presenting in the following sessions:

- **Session 4:** Nanomaterials and Nanotechnology for Electronic/Optoelectronic Devices and Sensors,
- **Session 5:** Nanomedicine, Nanosensor and Nano-biotechnology,
- **Session 6:** Nanotechnology for Energy Storage and Management,
- **Session 8:** Nanotechnology for Catalysis and Industrial Applications,
- **Session 9:** Nanotechnology for Startups and Industrial Enterprises, and
- **Special Session 1:** Advanced Nanostructured Materials for a Global Circular Economy.

We hope that these sessions will provide all participants insights into the current state of cutting-edge research work at VISTEC.

NanoThailand 2023 will provide all participants excellent opportunities to exchange ideas, network professionally, and broaden their knowledge. We hope that you all will have fruitful meetings and enjoy activities at Dusit Thani Hotel, the City of Pattaya, EECi and VISTEC during your excursion, as well as other places you visit in Thailand. Once again, on behalf of Vidyasirimedhi Institute of Science and Technology

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Minimally Invasive Glucose Monitoring with Molecularly Imprinted Polymer-Based Microneedle Biosensors

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Abstract:

Diabetes is typically diagnosed by monitoring blood glucose levels through invasive methods, offering critical health information. However, the accuracy of enzyme-based glucose sensors is constrained by variances in strip manufacturing, improper storage, and aging. To address these limitations, a molecularly imprinted polymer (MIP) sensor on microneedles (MN) has been developed for an electrochemical non-enzymatic approach to monitor glucose levels beneath the skin without the need for blood drawing. Employing a convenient photolithography method, a cross-shaped microneedle was fabricated using a non-cytotoxic bio-based resin derived from soybean oil and methyl methacrylic acid, demonstrating excellent mechanical properties. Electroless plating and sputtering methods were then utilized to coat the microneedle patch. Subsequently, the MIP membrane was deposited on gold microneedle electrodes using methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) as matrix materials in the presence of a glucose template. The microneedle MIP sensor effectively detected glucose in the range of 50 to 800 mg/dL via differential pulse voltammetry (DPV). This work presents a simple and effective sensing platform that overcomes the limitations of microneedle electrode fabrication and enzyme-based strip sensors, making it a promising tool for accurate and reliable non-invasive diagnosis in the future.

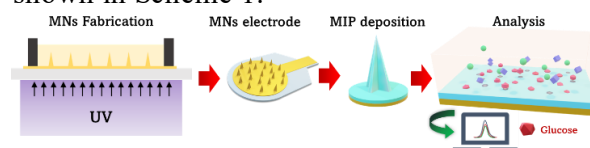
1. Introduction

Presently, the growing number of diabetes cases has led to an increased demand for and utilization of test strips. However, enzyme-based strips require careful storage in cool and dry places, inside a closed container, and away from direct light to maintain the accuracy and reliability of results¹. Moreover, pricking blood from fingertips using a lancet can cause significant pain and inflammation, posing a risk of infection.

Recently, the diagnostic utility of interstitial fluid (ISF) has increased to avoid the pain and limitations associated with withdrawing blood from fingers or using whole blood, as it contains biomarkers comparable to those found in blood². MNs are among the most suitable devices for accessing ISF due to their optimal length, typically ranging from 200 to 1500 μm ³. Therefore, the use of microneedles for transdermal glucose monitoring is highly feasible for conducting painless measurements⁴.

Herein, a biocompatible copolymer with photo-crosslinking properties has been synthesized for microneedle fabrication. Additionally, a suitable gold coating technique⁵ and deposition of molecularly imprinted polymers (MIPs) onto the microneedle electrode have been chosen due to

their key features, making them excellent receptors in biosensors for sensitivity and selectivity, as shown in Scheme 1.



Scheme 1. Schematic diagram of the fabrication process of microneedle MIP glucose sensor.

2. Materials and Methods

2.1 Materials

Acrylic acid (AAc), methacrylic acid (MAA), acrylated epoxidized soybean oil (AESO), methyl methacrylate (MMA), 2,2-dimethoxy-2-phenylacetophenone (DMPA), stearyl trimethyl ammonium chloride (SC), dimethylformamide (DMF), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), auric chloride (HAuCl_4), potassium hexacyanoferrate (III), and potassium hexacyanoferrate(II) trihydrate were obtained from Sigma-Aldrich (St. Louis, MO, USA). D-glucose and potassium chloride (KCl) were obtained from Kanto Chemicals (Chuo-ku, Tokyo, Japan).

2.2 Synthesis of AESO Resins

AESO-based resins were synthesized to create MN arrays and substrate sheets for the MN



patches. The resin for microneedle's substrate (B-resin) was formulated by dissolving 100 mg of DMPA in 2 mL of AAc until a homogeneous mixture formed, which was then poured into AESO (8 mL). The MN arrays resin (MN-resin) was prepared by dissolving 100 mg of DMPA in 3 mL of MMA and then poured into AESO (7 mL). All resins were stirred for 24 hours in a dark room at room temperature, covered with aluminum foil, and stored at room temperature before use.

2.3 Photomask Preparation

A photomask was employed to block UV radiation, preventing photopolymerization beyond the zones of the microneedle array. Initially, a glass slide was cleaned and sputtered with a 40 nm thick layer of aluminum on one side. Subsequently, cross-shaped micro-windows with a diameter of 400 μm were etched onto the aluminum film using a low-energy laser.

2.4 Preparation of Microneedle Patches

The microneedle's substrate was created by pouring 100 μL of B-resin over a photomask slide, covering it with a transparent plastic sheet with a 0.2 mm spacer, and exposing it to 10 seconds of UV irradiation. MN-resin was then filled into a PDMS frame and exposed to UV irradiation from beneath for 120 seconds, as depicted in Scheme 1. Subsequently, 3D MN arrays were formed and rinsed three times with ethanol and distilled water to eliminate non-polymerized monomers, before undergoing an additional 120 seconds of UV exposure to complete the curing reaction.

2.5 Microneedle Electrode Coating Process

Electroless plating and sputtering methods were employed to deposit a gold layer onto the 3D structure of the microneedles (MNs), creating a working electrode for sensor devices. The MN patches were immersed in a 0.1% solution of stearyl trimethyl ammonium chloride (SC) for 10 seconds to deposit a positively charged surface. Next, the MN patches were immersed in a Pt colloid for 60 seconds, enabling Pt nanoparticles to spontaneously adhere to the surface through electrostatic contact between the cationic charge-modified substrate and the negatively charged Pt colloid particles. The remaining free Pt particles were gradually removed by rinsing them with distilled water. Subsequently, the MN patches were placed in a plating tube containing 10 mM HAuCl_4 , and 20 mM H_2O_2 was added while shaking the plating tube for 5 minutes. The

electrodes were then dried at 50 $^\circ\text{C}$ for 2 h. Finally, a gold-sputtering process was performed at a current of 50 mA to achieve a film thickness of 100 nm. Once the desired thickness was reached, the MN electrodes underwent annealing at 70 $^\circ\text{C}$ in an oven for 3 h to ensure a uniform coating.

2.6 Cytotoxic Assay

L929 cells (American Type Culture Collection, Manassas, VA, USA) were cultured in Dulbecco's modified Eagle's medium (Sigma-Aldrich, St. Louis, MO) supplemented with 10% heat-inactivated fetal bovine serum in a humidified atmosphere of 5% CO_2 at 37 $^\circ\text{C}$. Before *in vitro* cytotoxicity testing, 100 mg of cured MN-resin was immersed in 1 mL of cell culture medium. The cytotoxicity assay was conducted using the MTT method in a 96-well plate. Subsequently, 1×10^3 cells in 0.1 mL of culture media were seeded in a 96-well plate. After 72 h of incubation, 0.1 mL of culture medium containing different concentrations of the extracted polymers was added to the 96-well plate. Following an additional 24 h of re-incubation, 0.1 mL of the MTT solution (300 $\mu\text{g/mL}$) was added to each well, and the cells were incubated for an extra 3 h. After discarding the medium, 0.1 mL of DMSO was added to dissolve the generated purple formazan crystals. The number of viable cells was determined at 540 nm.

2.7 Porcine Skin Insertion Tests

The penetration performance of MNs was evaluated using porcine skin as a model. Fresh porcine skin was obtained from the pig's back area, sliced into 3-4 mm thickness, and stored at -3 to -5 $^\circ\text{C}$. Prior to use, the frozen porcine skin was placed in a bag and thawed in water at room temperature. A skin slice was positioned on a flat surface, and the MN electrode was inserted using a thumb-pressing force for 20 seconds.

2.8 MIP Electropolymerization

The gold MN electrodes were initially cleansed with ethanol and PBS. For the second cleaning step of the gold surface, Cyclic voltammetry (CV) was performed with a scanning rate of 50 mV/s in PBS (pH 7.4), containing 0.1M KCl, 2.5 mM $\text{K}_3\text{Fe}(\text{CN})_6$, and 2.5 mM $\text{K}_4\text{Fe}(\text{CN})_6$. This process utilized a three-electrode system for 10 cycles or until a stable signal was obtained. Subsequently, 50 μL of 0.05 M allyl mercaptan in a 50% v/v ethanol/water solution was applied to the gold MNs electrodes within a closed container. The reaction proceeded for 30 min. The modified

substrate was washed with ethanol and then dried in an oven at 50 °C to eliminate the solvent. MIP solution was prepared by mixing two solutions of glucose (40 mg) and KCl (0.1 M) with 1 ml PBS in 9 ml DMF. A functional monomer MAA (93 μ L), crosslinker EGDMA (335.27 μ L), and AIBN (50 mg) and DMPA (50 mg) initiators were added to the solution. N₂ gas was bubbled in the mixed solution for 5 min, then stirred for 2 h. The MIP layer was deposited via electropolymerization by CV (10 cycles) with the three-electrode system in a potential range of -400 to +600 mV vs. Ag/AgCl at a scan rate of 50 mV/s. After completing the electropolymerization process, the resulting polymer was exposed to UV irradiation for 5 min to ensure full curing, followed by drying at 50 °C for 30 min. The materials were rinsed with ethanol to remove the uncured monomer. Finally, the glucose template molecules were removed from the polymer matrix film by dripping it with acetic acid (20 mM) in acetonitrile (20% in water) for 30 min. A control polymer substrate (non-imprinting polymer, NIP) was prepared with the same procedure described above without glucose.

2.9 Electrochemical Measurements

CV was employed to evaluate the performance of the modified MN electrodes. The experiment was conducted using the three-electrode system consisting of Ag/AgCl (RE), Pt (CE), and the modified microneedle electrode (WE) at a scan rate of 10-200 mV/s. Differential pulse voltammetry (DPV) was explored with the same three-electrode system, ranging from -0.1 to 0.6 V, with a modulation amplitude of 0.025 V, modulation time of 0.005 seconds, step of 0.005 V, and interval time of 0.1 seconds. All electrochemical measurements were carried out in a solution containing 0.1M KCl, 2.5 mM K₃Fe(CN)₆, and 2.5 mM K₄Fe(CN)₆.

3. Results and Discussion

3.1 Microneedle Patch Fabrication Process

A thin sheet substrate, with a fixed thickness of approximately 200 \pm 20 μ m, was fabricated from B-resin to control the intensity of UV light passing through micro-sized windows. This ensures uniform maintenance of microneedle length, height, and shape. The microneedle design, featuring a four-point star shape, aims to reduce the wound size at the insertion site compared to cones or pyramids. The four-points star shape, with a higher surface area than squares or circles based of

the same dimensions and height, enhances sensor modification on this microneedle type, providing more reaction sites and generating a larger signal, as shown in Figure 1.

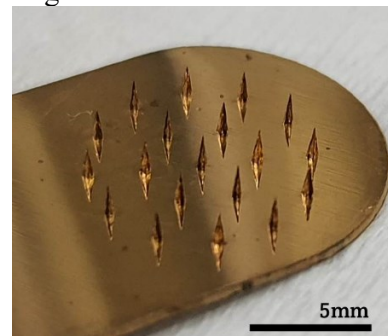


Figure 1. The appearance of the MN electrode.

3.2 Surface Coating of Microneedles

The electroless plating method resolves shadow issues encountered with the sputtering method. A continuous gold thin film is formed at room temperature due to the excellent catalytic properties of the Pt nanoparticles. Figure 2A displays the initial layer of gold deposited through electroless plating, with gold nanorods approximately 10–20 nm in diameter and 50–100 nm long. Subsequently, the electrode underwent gold nanoparticle sputtering, resulting in a 100 nm thick gold film deposition. Larger-sized gold particles were observed after the second layer of deposition, ranging from about 60–300 nm, as shown in Figure 2B. Figure 2C illustrates the two stages of the gold nanoparticle coating process, covering the entire area of the microneedle electrodes, particularly at the tip and base of the microneedles. Figure 2D shows the finished MN electrode with a resistance value lower than 3 Ohms, measured from the furthest MN tip on the left to the furthest connector on the right.

3.3 Microneedle Insertion study

The microneedle's in vitro skin insertion behavior was investigated on a slice of porcine skin. The microneedles penetrated to a depth of around 300-400 μ m, as seen in Figure 3A, Given that porcine skin is harder, thicker, and fatter than human skin, the microneedle electrode has sufficient penetrating capability for use with human skin.

3.4 Cytotoxicity Tests

The IC₅₀ (the concentration at which 50% of the cells are killed) was not observed for any concentration in the extract medium concentrations, as shown in Figure 3B. Therefore, the MN materials are highly biocompatible and can

be safely used in living organisms for transdermal applications.

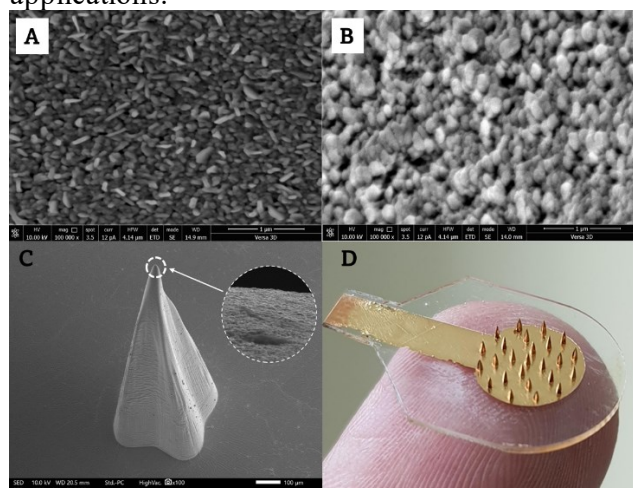


Figure 2. SEM images of gold layers on the MNs electrode by; (A) The first layer of the electroless plating, (B) the second layer of the sputtering method, (C) A full coverage of gold nanoparticles on the microneedle electrode, (D) appearance of the resulting microneedle electrode.

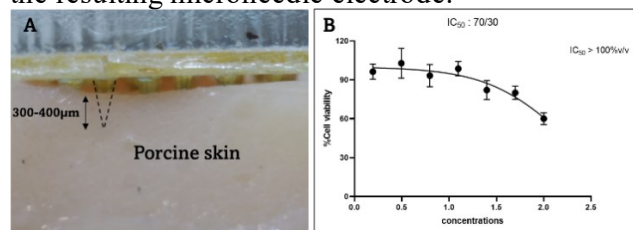


Figure 3 The insertion behavior of the microneedle electrode on porcine skin (A) cross-section view, (B) MTT assay to determine the IC_{50} value of microneedle material extracts at different concentrations.

3.5 MIP Microneedle Electrode Behavior

The performance of the MIP MN glucose sensors and electrode were evaluated. The allyl mercaptan-modified electrode (curve b) shows a lower oxidation peak compared to the bare electrode (a), attributed to the presence of a vinyl group layer, as depicted in Figure 4A. The lowest oxidation peak is observed in MIP (curve c) before the template is removed, indicating a thicker polymer block for electron transfer. After removing the template, curve d exhibits a distinct oxidation peak in MIP, suggesting an increase in the degree of electron transfer. The effects of scan rate on the electrochemical behavior of glucose at the glucose MIP MN sensors were investigated by CV. With increasing the scan rates in 50 mg/dL glucose, the anodic peak currents increased, and the peak potential moved slightly in a more

positive direction. An anodic (I_{pA}) and cathodic (I_{pC}) peak currents are linearly proportional to the square root of the scan rate ($v^{1/2}$, V/s) over the range of 10 to 200 mV/s, as shown in Figure 4B. The linear regression equations are $I_{pA} = 1.0206v^{1/2} + 0.0455$, ($R^2 = 0.9989$) and $I_{pC} = -1.2531v^{1/2} - 0.0052$, ($R^2 = 0.9928$), respectively. Thus, anodic and cathodic currents are diffusion-controlled processes and reversible electron transfer kinetics at the MIP MNs sensor.

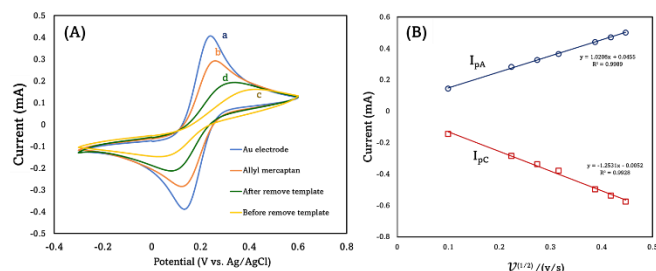


Figure 4 (A) CV plots of (a) gold electrode, (b) Allyl mercaptan modified electrode, (c) MIP before removing the template, and (d) MIP after removing the template, at a scan rate of 50 mV/s. CV plots of the MIP microneedle electrode, (B) A linear relationship plot of the anodic (I_{pA}) and cathodic peak current (I_{pC}) vs. the square root of the scan rate using 25 mg/dL glucose solution, all measurements were performed in PBS (pH 7.4) containing 0.1M KCl, 2.5 mM $K_3Fe(CN)_6$ and 2.5 mM $K_4Fe(CN)_6$.

3.6 Voltammetric Detection of MIP and NIP MNs Sensor

DPV measurements were conducted by scanning from -0.1 to 0.5 V. At each step, the template was removed for the next measurement by rinsing it with distilled water and immersing the electrode in 5 mL of acetic acid (20 mM) in acetonitrile (20% in water) for 5 min. Figures 5A and 5C illustrate the DPV and peak current plots of the MIP microneedle sensor at various glucose concentrations. The peak current shifts toward higher potentials (from 0.0192 V to 0.0237 V) as glucose molecules bind to the imprinted site and block electron transfer. With increasing glucose concentrations, the peak current of the MIP microneedle sensor decreases significantly. The electrochemical signal logarithmically reduces up to 800 mg/dL, represented by $y = -0.01\log(G) + 0.0019$, $R^2 = 0.9766$, as shown in Figure 5D. The linear range of the MIP microneedle glucose sensor is 50-800 mg/dL, suitable for applications in hyperglycemia and type 1 diabetes. The NIP sensor served as a standardized comparison with

the MIP sensor, both assembled from the same monomer and crosslinker to confirm that the NIP sensor does not react with any analyzer. DPV peak currents, as shown in Figure 5B, indicate that the curves remain relatively stable in the same range of glucose concentrations compared to the MIP sensor. Additionally, all peak currents generated from the NIP microneedle electrode do not shift to a higher potential as glucose concentrations increase.

4. Conclusions

The MIP glucose sensor based on a microneedle electrode has been successfully developed, utilizing a novel and convenient fabrication process with a bio-based and bio-compatible resin derived from soybean oil. This process enables efficient and rapid production of microneedle patches within 5 minutes, with high

potential for scalability to industrial production. Gold electroless plating and the sputtering method were effectively employed to coat a conductive layer, addressing incomplete coverage issues inherent in microneedle-based systems. The microneedle (MNs) sensors exhibit outstanding mechanical characteristics, enabling penetration for the analysis of chemicals in interstitial fluid (ISF). The MIP microneedle sensor measurements demonstrate a linear relationship between ΔI and $\log(\text{glucose concentration})$ for DPV, within a range of 50 to 800 mg/dL, indicating the suitability of these sensors for point-of-care testing (POCT). MIP-based biosensors on microneedles present a promising solution to overcome the limitations of enzyme-based sensors, especially concerning temperature effects, and offer non-invasive monitoring.

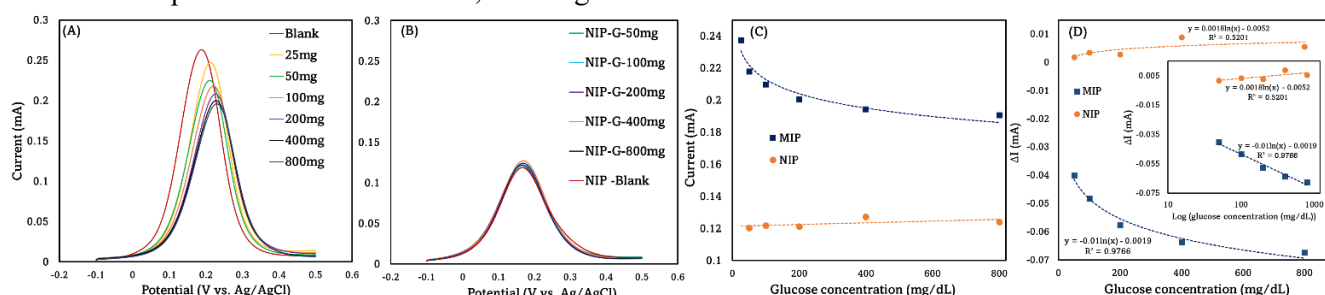


Figure 5. DPV curves of (A) MIP-1 microneedle electrode, (B) NIP at different glucose concentrations. (C) Relationship between changes in the peak current and glucose concentration. (D) A calibration plot of the linear relationship between the change in peak current and the log (glucose concentration).

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Chitosan Blending with Water-Soluble Polymers as Dissolving Microneedles for Controlled Drug Release

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Abstract:

Chitosan has gained significant interest due to its ability to film-forming, biodegradability, and biocompatibility, making it suitable for topical and transdermal drug delivery such as fabricating microneedles. In this study, chitosan microneedles were prepared by incorporating (PVP) and (PVA) in ratios (1:1, 2:1, and 3:1 chitosan: polymers) to control drug release. The mechanical properties were tested using the universal testing machine (UTM), and the skin penetration ability was tested using pig skin (*ex vivo*). The results indicated that the microneedles exhibited sufficient strength to penetrate the outer layer of the porcine skin effectively. The study included incorporating two drugs: 13% w/w of curcumin as a model of hydrophobic drugs, and 32% w/w of butterfly pea extract as a model of hydrophilic drugs. Chitosan blended with PVP demonstrated the ability to finely tune the release profiles of both hydrophobic and hydrophilic drug models, with approximately 60% of hydrophilic and 48% of hydrophobic loaded drugs over two days. In contrast, chitosan blended with PVA did not exhibit a significant difference from the blank microneedles, releasing 49% of the loaded drugs over the same time frame. Chitosan microneedles incorporating PVP are a promising candidate for controlled transdermal drug delivery.

1. Introduction

Dissolving microneedles DMNs are usually made of biodegradable or dissolving polymers and have attracted a lot of curiosity in recent years ¹⁻³. Nevertheless, these microneedles disintegrate fast when they come into touch with moisture in the skin, which causes speedy drug distribution. Drugs can be effectively delivered into the skin using microneedles consisting of natural polymers such as hyaluronic acid (HA), polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), and maltose ⁴. Carboxymethyl cellulose (CMC) ⁵ and Chitosan are modified natural polymers. Synthetic polymers such as PLGA⁶. Extended drug release may be possible using biodegradable microneedles composed of copolymer poly(lactic-co-glycolic acid) (PLGA) ⁷. PLGA is a family of FDA-approved biodegradable polymers that are physically durable and biocompatible and have been researched as a drug delivery vehicle for numerous medicines, proteins, and macromolecules ⁸. PLGA can potentially be used in a long-term drug delivery system ⁹ its degradation rate can vary from weeks to several months to a year ^{10, 11}. However, PLGA is expensive and dissolves in an organic solvent such as dichloromethane¹². This solvent is incompatible with silicone mold, making it difficult to utilize as a structural material for DMNs. PLGA has been

blended with PVP to fabricate microneedles and tune the drug release for two weeks ¹³. To overcome the limitations of PLGA, Chitosan-based delivery methods have benefits over other hydrophobic polymers such as PLGA for the encapsulation of biopharmaceuticals since it does not require organic solvents. It is cost-effective and degrades between weeks to months ^{14, 15}. Chitosan β -(1 \rightarrow 4)-linked D-glucosamine and N-acetyl-D-glucosamine is a family of molecules with variations in their composition, size, and distribution of monomers rather than a single polymer with a well-defined structure ¹⁶. Chitosan's biocompatibility, degradability, and nontoxicity have made it a popular drug delivery material. Chitosan matrix swelling and disintegration can release drugs contained in chitosan carriers, producing sustained-release action^{14, 17}. Its safety as dietary supplements or medication carriers has been proven in animal and human models. Chitosan is a biocompatible polymer that is often utilized in delivery methods to help the formulation's wound-healing benefits ¹⁸. The demonstration of material with the desired drug release rate could be achieved through the adjustment of the ratio between chitosan and water-soluble polymers such as PVP and PVA. This study aims to develop DMN patches made of chitosan blended with PVA and PVP for tunable and sustained release of hydrophobic and hydrophilic drugs.

2. Materials and Methods

2.1 Materials

Chitosan (deacetylated 85%), MW 30,000 was purchased from Seafresh Chitosan (lab) Co. Ltd. Thailand; Poly (vinyl alcohol) (PVA), MW 95,000; Polyvinylpyrrolidone (PVP) MW 40,000 were purchased from Sigma Aldrich. Glacial Acetic Acid (A.A) 99% and Sodium Hydroxide of analytical reagent grade were purchased from Emsure Co. Curcumin MW 368.38 was purchased from ACROS Co. Butterfly pea powder HQ was purchased from Tipco, Thailand Biotech Co. Ethanol was purchased from Sigma Aldrich. Polydimethylsiloxane molds (PDMS): (1.6 cm in diameter, containing 277 needles arranged with a tip-to-tip distance of 1150 μm ; each needle is nail-shaped with 350 \times 350 \times 360 μm^3 (W \times L \times H) square column and 500 μm high of the square pyramid on the top). The mechanical properties were measured by universal testing machine UTM, Shimadzu EZ-S, Shimadzu Corporation, Tokyo, Japan. The penetration ability was measured by using commercial porcine ear skin.

2.2 Synthesis

For the microneedle matrix, chitosan powder was dissolved in a 0.2 M aqueous solution of acetic acid to obtain a 3% (w/v) chitosan solution. The obtained viscous chitosan solution was then neutralized by adding drops of sodium hydroxide 0.5 M after that dialyzed at room temperature against deionized (DI) water with several water exchanges to remove excess acetic acid and salt (final pH approximately 5). 6% (w/v) of chitosan solution mixed with 9% (w/v) of HA, PAA, PVA, PVP, trehalose, and sucrose Table 1. The mixture was poured into the PDMS and dried overnight. Curcumin was dissolved with ethanol and loaded to the mold to make 13% w/w the maximum capacity of loading. Butterfly pea was dissolved with water and loaded to the mold to make 33% w/w the maximum capacity of loading.

2.3 Characterization

The needles with drugs and without drugs were applied onto the porcine skin to study the penetration efficiency. Mechanical compression

tests were performed using a UTM. A microneedle array was placed on a stainless-steel base plate's

Table 1. The amount of mixing between chitosan: polymers and sugars

Formations	CS: polymers & sugars	mg of materials	
		CS	polymers & sugars
1	1:1	45	45
2	2:1	60	30
3	3:1	67.5	22.5

flat inflexible surface. An axial force was applied by a moving sensor mount, perpendicular to the axis of the microneedle array, at a constant speed of 150 mm/min¹⁹. *In vitro* drug release has been studied. Briefly, needles with drugs were immersed in 100 ml PBS (pH 7.4) and a water jacket was used to control temperature at 37 °C. The drug solution released was acquired at predetermined time intervals (0, 0.25, 0.5, 01, 02, 04, 08, 12, 24, and 48 hours) through the sampling port and then measured using a UV machine. A comparison between the two groups was performed using ANOVA: single factor using statistical software (Graph Pad Prism 9). Data presented as mean \pm SD. A difference of $P < 0.05$ was considered statistically significant.

3. Results

3.1 Fabrication of chitosan- HA, PAA, PVA, PVP, Trehalose and Sucrose

Sugars blended with chitosan showed brittle needles when the chitosan was the major component and sticky when the sugars were the major component. Sugar molecules are known to increase polymers' flexibility and water absorption capacity. This can lead to increased stickiness, especially in humid environments. The stickiness of microneedles could impact their handling and storage. It might also affect their ability to pierce the skin effectively if they adhere to the skin surface. The results showed a precipitate when HA and PAA blended with chitosan due to the difference in pka value at pH 5.0.

Blending chitosan with PVA and PVP showed good results. Increasing chitosan in microneedle formulation likely played a significant role in the transition from hollow to solid microneedles. Chitosan is known for its structural integrity and rigidity. This transition

may have occurred due to chitosan's ability to form a solid matrix when it interacts with the other polymers (PVA and PVP) in the formulations.

3.2 Drug-loading and skin penetration (ex vivo)

Curcumin has been loaded as a hydrophobic drug model. It was loaded to the formulation of chitosan: PVP and pure chitosan with a maximum loading capacity of 13% w/w.

Table 2. The effect of drug on the penetration efficiency

Formulation Wt. CS: wt. polymers	Drug loading and penetration efficiency	
	Curcumin w/w 13 %	Butterfly pea w/w 32%
CS	Curcumin enhanced the penetration	Good penetration
1 CS: 1 PVP	Curcumin enhanced the penetration	Good penetration
2 CS: 1 PVP	Curcumin enhanced the penetration	Good penetration
3 CS: 1 PVP	Curcumin enhanced the penetration	Good penetration
1 CS: 1 PVA	-	Good penetration
2 CS: 1 PVA	-	Good penetration
3 CS: 1 PVA	-	Good penetration

On the other hand, the formulation of chitosan: PVA didn't encapsulate curcumin. Butterfly pea extract has been loaded as a hydrophilic drug model. It was loaded to the formulation of chitosan: PVP, chitosan: PVA, and pure chitosan with a maximum loading capacity of 32% w/w Table 2. Besides mechanical property tests, we tested the insertion ability of the DMNs in porcine skin ex vivo. The needles successfully penetrate the porcine skin with different depths due to the different formulas and ratios.

The results show that the chitosan: PVP and pure chitosan formulations are suitable for the encapsulation of hydrophobic drugs like curcumin. However, chitosan: PVA formulation did not successfully encapsulate curcumin. This means

that the combination of chitosan and PVA may not be suitable for encapsulating hydrophobic drugs like curcumin under the conditions or methods used in this study. Chitosan-based formulations can effectively encapsulate hydrophilic drugs. Interestingly, the results reveal that pure chitosan, without the addition of PVP or PVA, was able to encapsulate butterfly pea extract effectively.

The experiment successfully demonstrated that the needles penetrated the porcine skin to different depths. This variability in penetration depth suggests that the composition of the needles, as well as the ratios of the components in the patches, have an impact on how deeply the needles can penetrate the skin. The results indicated that the depth of the whole needles in all the ratios is more than 600 μm which is good enough to penetrate the stratum corneum reaching the epidermis layer. The statistical analysis approved that adding butterfly pea extract as a hydrophilic drug model didn't significantly affect the depth of the needles compared with adding curcumin. DMNs with curcumin penetrated deeper into the porcine skin.

3.3 Penetration efficiency

To overcome the barrier of the skin and deliver the drug efficiently into the skin, the mechanical property and the insertion ability are critical for DMNs. In brief, the DMN sample applied to the porcine ear skin and the needle's high and depth has been measured to assess the penetration efficiency. As shown in Figure 1, all microneedles penetrate the skin successfully. This result contributes to the overall understanding of microneedle technology and its potential for various medical and pharmaceutical applications.

3.4 Drug release in vitro

Chitosan sustains the release of butterfly (hydrophilic drug model) where around 44 % w/v has been released after 2 days from pure chitosan. chitosan blended with PVA showed faster drug release with increasing concentrations of PVA in the needles around 49%, 47%, and 46% w/v 1:1.

2:1, 3:1 CS: PVA respectively released after 2 days. the drug release decreased with the concentration of PVA. PVP blended with chitosan showed the fastest drug release 69%, 67%, and 48% w/v, from the ratio CS: PVP 1:1, 2:1, 3:1 respectively Fig. 2a.

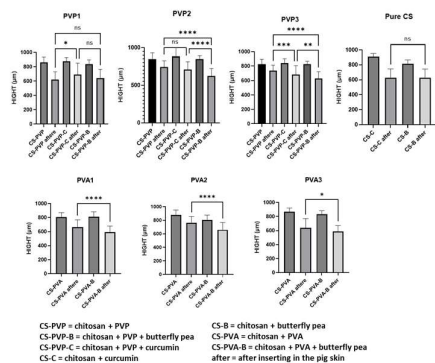


Figure 1. Statistical analysis of the needles' height in the patches and the needles' depth in porcine skin (PVP1 1:1 CS: PVP, PVP2 2:1 CS: PVP, PVP3 3:1 CS: PVP), (PVA1 1:1 CS: PVA, PVA2 2:1 CS: PVA, PVA3 3:1 CS: PVA), and pure CS (only chitosan with drugs, no polymers blended with chitosan). p-value control using ANOVA-single factor data analysis, <0.05 is considered statistically significant.

PVP is known for its solubilizing properties and ability to enhance drug release. The high drug release observed with CS: PVP blends, especially at the 1:1 ratio, indicates a strong influence of PVP on accelerating drug release 26. CS: PVP blends outperform CS: PVA blends in terms of drug release rate. This could be attributed to the distinct properties of PVP, which promotes rapid drug dissolution and diffusion 27. CS: PVP loaded with curcumin showed sustain release 55%, 45%, 39%, and 22% w/v from the ratio CS: PVP 1:1, 2:1, 3:1, and pure CS respectively Fig. 2b.

Conclusion

The incorporation of chitosan into blends with PVA and PVP in varying ratios has proven to be a promising approach for tunable drug release systems. The successful fabrication of composite needles with excellent mechanical strength, as determined by the Universal Testing Machine (UTM). Furthermore, the penetration of these

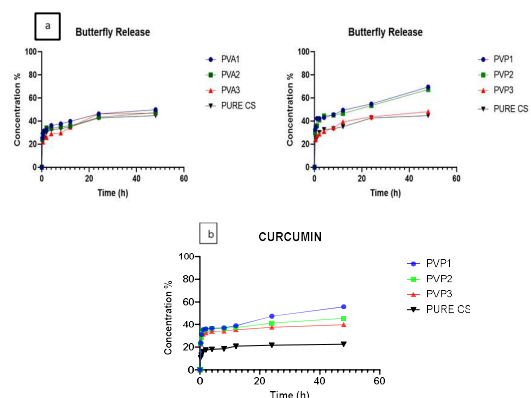


Figure 2. In vitro release profile of a) butterfly pea extract in CS: PVA (PVA1 1:1, PVA2 2:1, PVA3 3:1) and CS: PVP (PVP1 1:1, PVP2 2:1, PVP3 3:1), b) curcumin in CS: PVP (PVP1 1:1, PVP2 2:1, PVP3 3:1) patches

formulations through porcine ear skin demonstrates their potential for intradermal and transdermal drug delivery. The noteworthy finding in this study is the variation in drug release kinetics observed between chitosan-PVA and chitosan-PVP blends. After two days of testing, chitosan blended with PVP exhibited a notably faster drug release rate compared to chitosan-PVA blends. This suggests that the choice of polymer partner plays a crucial role in fine-tuning drug release profiles. These results underscore the importance of carefully selecting and optimizing the polymer blend composition to achieve the desired drug release characteristics. The versatility of chitosan as a biomaterial, when combined with appropriate polymers, opens up exciting possibilities for tailoring drug delivery systems to meet specific therapeutic requirements. Further research in this field could explore the potential applications of these formulations in controlled drug release for various medical scenarios

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CHARGE TRANSPORT PROPERTIES IN METAL HALIDE HYBRID PEROVSKITES: THE PERSPECTIVE OF LARGE POLARONS AND ALLOY SCATTERING

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Abstract

Metal halide hybrid perovskites (MHPs) have drawn much attention due to the rapid progress in perovskite solar cells and their intriguing fundamental photophysical properties. Based on an initial power conversion efficiency (PCE) of 3.8%, they demonstrated a certified PCE of 26%. In MHPs, lead-halide and lead mixed-halide perovskites are forefront material systems with tunable electrical and optical properties. Charge-carrier mobility is an important factor that strongly affects the PCE of perovskite solar cells. However, a detailed understanding of the underlying transport mechanisms of these perovskite materials remains incompletely understood. Herein, we derive models of charge transport based on large polarons and alloy scattering to calculate charge-carrier mobilities and elucidate the transport mechanisms. The calculated RT mobility values were in very good agreement with the experimental results measured using an optical pump terahertz probe technique. In lead-halide perovskites, large polaron transport dominated the transport mechanism. Both large polaron transport and alloy scattering were dominant in lead mixed-halide perovskites.

1. Introduction

Metal halide perovskites (MHPs) have been widely investigated due to their potential applications in next generation photovoltaics.^{1,2} This interest stems from both their advantageous optical and transport properties, which include high absorption coefficients, high charge-carrier mobilities and relatively long charge-carrier diffusion lengths, as well as high defect tolerance. Lead-halide and lead mixed-halide perovskites with the formula ABX_3 ($A = FA^+, MA^+, Cs^+$; $B = Pb^{2+}$; $X = I, Br$) are prototypical photoactive materials for perovskite solar cells (PSCs). An initial power conversion efficiency (PCE) of 3.8% has been demonstrated for a single-junction PSC based on $MAPbI_3$.³ Up until now, a PCE of 26.1% has been certified.⁴

In charge-carrier mobility measurements, a room-temperature (RT) charge-carrier mobility is obtained using an optical pump terahertz probe (OPTP). This spectroscopy technique uses an optical pulse to create both free electrons and holes as well as a terahertz pulse to analyze the transport properties of charge carriers. The experimental results of RT mobility have been measured, such as in lead-halide perovskites,⁵⁻⁷ $MAPbI_3$ (35 cm^2/Vs), $FAPbI_3$ (27 cm^2/Vs), $FAPbBr_3$ (14 cm^2/Vs), $FA_{0.83}Cs_{0.17}PbI_3$ (40 cm^2/Vs), $FA_{0.83}Cs_{0.17}PbBr_3$ (10 cm^2/Vs), and lead mixed-halide perovskites,⁷ $FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)_3$ where $x = 0.3$ (24 cm^2/Vs), $x = 0.4$ (19 cm^2/Vs), $x = 0.5$ (15 cm^2/Vs), $x = 0.6$ (13 cm^2/Vs), and $x = 0.7$ (12 cm^2/Vs). However, a detailed explanation of these RT mobilities and underlying

transport processes is still incomplete, both in lead-halide and lead mixed-halide perovskites.

In this work, we report an understanding of the transport properties of charge carriers in MHPs. We provide transport models of charge-carrier mobility that account for large polarons and alloy scattering to calculate the RT mobilities. Theoretical results were comparable to the experimental data.⁵⁻⁷ It was found that these calculated results provided very good agreement with the experimental data measured using OPTP. Large polarons and alloy scattering provide the background transport mechanisms for redesigning strategies to provide efficient PSC absorption material development.

2. Methods and transport models

Based on OPTP, charge-carrier mobility can be determined from the product of the quantum yield of photon-to-charge conversion and sum of both electron and hole mobilities,⁸ $\phi \sum \mu$, where $0 \leq \phi \leq 1$ and $\sum \mu = \mu_e + \mu_h$. From a theoretical perspective, carrier mobility is determined using $\mu = e\tau_{tr}/m^*$, where e is the elementary charge, τ_{tr} is the momentum relaxation time, and m^* is the effective mass of charge carriers (m_e^* for an electron and m_h^* for a hole). The effective mobility related to multiple scattering mechanisms can be calculated by Matthiessen's rule, $\mu_{tot}^{-1} = \sum_i \mu_i^{-1}$.

A brief review of transport models is presented, including large polarons and alloy scattering, to investigate RT mobility. First, a large polaron (LP) transport consists of a charge-carrier

coupled with a longitudinal optical (LO) phonon, with a polaron binding energy of $E_P = 0.106\alpha^2\hbar\omega_{LO}$ and a polaron radius of $L_P = \sqrt{\hbar/2m^*\omega_{LO}}$, based on a Fröhlich polaron theory. When an electron (or a hole) moves in a lattice, an ionic crystal polarization is created that follows the charge carrier motion, as shown in Figure 1(a). In Figure 1(b), a large polaron is formed, and a dressed particle is produced by a carrier coupled with an LO phonon cloud created from self-induced polarization. The carrier-phonon coupling constant describes the interaction strength between a carrier and LO phonons, $\alpha = \frac{e^2}{\hbar} \sqrt{\frac{m^*}{32\pi^2\varepsilon_0^2\hbar\omega_{LO}}} \left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \right)$, where $\hbar\omega_{LO}$ is the effective LO phonon energy, ε_s is the static dielectric constant and ε_∞ is the high-frequency dielectric constant. Thus, the large polaron mobility is given by^{9,10}

$$\mu_{LP} = \frac{e}{2\alpha\omega_{LO} m^* (1+\alpha/6)^3} f(\alpha) (e^{\hbar\omega_{LO}/k_B T} - 1). \quad (1)$$

The slowly varying function, $f(\alpha)$, is assumed to be unity.

Second, alloy scattering (AL) is a perturbative process where different atoms are randomly distributed inside the same lattice site. A random distribution of various atoms in lead mixed halides, *i.e.*, Br⁻ atoms substituted in I⁻ sites or *vice versa*, produces an alloy scattering potential (U). A simple model of the alloy scattering model is depicted in Figure 2. The alloy scattering strength is influenced by the concentration fraction of the alloying atoms (x), in which charge carriers scatter by randomly positioning various atoms or alloying atoms.¹¹ The alloy scattering mobility depends on the alloy scattering potential, thermal energy ($k_B T$), and volume of a unit cell related the lattice constant ($\Omega = a^3/4$). The mobility formula is given by¹¹

$$\mu_{AL} = \frac{16e\pi^{1/2}\hbar^4}{3(2m^*)^{5/2}\Omega U^2 x(x-1)(k_B T)^{1/2}}. \quad (2)$$

3. Results and discussion

In charge-carrier mobility calculations, we first examine the principle constant parameters, *i.e.*, m_e^* , m_h^* , ε_∞ , ε_0 , $\hbar\omega_{LO}$ and a , for numerical evaluations of Eqs. (1) and (2). Table 1 shows the constant parameters for lead halides and lead mixed halides, respectively. To validate our

transport models, theoretical results are compared with RT mobility data measured using OPTP spectroscopy. Nevertheless, to compute the alloy scattering mobility in Eq. (2), it is challenging to measure the alloy scattering potential and it needs to be specified as a fitting parameter. Calculated results for the Fröhlich coupling constant and RT charge-carrier mobility, as well as the experimental results, are presented in Tables 2 and 3 for lead-halide and lead mixed-halide perovskites, respectively.

We use the large polaron mobility in Eq. (1) to describe charge transport in lead-halide perovskite films, MAPbI₃, FAPbI₃, FAPbBr₃, FA_{0.83}Cs_{0.17}PbI₃, and FA_{0.83}Cs_{0.17}PbBr₃. In Table 2, calculated results of RT mobility are in very good agreement with experimental data. The results suggested that the large polaron transport model explains charge-carrier mobility well in lead halide films. Therefore, the polaronic effect has a major influence on the charge transport properties of MHPs. The calculated polaron binding energies and large polaron radii in MHPs are shown in Table 4. The binding energies of polarons, which range from 7.0 to 22.8 meV, are less than the thermal energy of 26 meV at room temperature (300 K). The large polaron radii between 24 and 40 Å are significantly greater than those of the PbI₃ octahedron (6.2 Å). These results suggest that the large polaronic effect has a band-like transport characteristic, where the carrier mobility decreases with increasing temperature, $\mu_{LP} \propto T^{-m}$,^{5,9} and atomic screening with a high tolerance to defects⁵, respectively.

The alloy scattering potential in FA_{0.83}Cs_{0.17}Pb(I_{1-x}Br_x)₃ is caused by a random distribution of Br⁻ atoms in the I⁻ atom lattice sites. The polaronic effect is simultaneously dominant. Thus, we combine both transport mechanisms based on Matthiessen's rule, $\mu_{tot} = (\mu_{LP}^{-1} + \mu_{AL}^{-1})^{-1}$, to examine charge-carrier mobility. In Table 3, theoretical calculations using the alloy scattering potential of $U = 3.0$ eV¹¹ provided good quantitative agreement with the experimental data. It is shown that the scattering from both LO phonons and alloy disorders are dominant scattering mechanisms. The strength of alloy scattering is determined by a concentration fraction factor, $x(x-1)$. This factor yields a minimal mobility value at $x = 0.5$. This indicates a relatively significant alloy interaction at limiting Br compositions with I/Br ratios closer to 1:1. The

mobility of an alloying system is lower than that of a pure compound. For this reason, alloy scattering cannot be ignored when analyzing the properties of charge transport in lead mixed-halide perovskites.

Based on this information, we can describe charge transport dynamics in MHPs. Through photoexcitation, hot carriers are generated (Process-1: carrier generation). These hot carriers rapidly relax to form free charge carriers in a scattering process *via* LO phonon emissions within a cooling time of 100 fs (Process-2: carrier relaxation). Free charge carriers, both electrons and holes, interact with LO phonons generated from self-induced polarization, leading to formation of large polarons within ~2 ps (Process-3: large polaron formation). Large polarons propagate through a material and scatter when they contact scattering sources (Process-4: charge scattering).

4. Conclusion

We examined charge-carrier mobilities in the metal halide hybrid perovskites. The calculated RT mobilities between 11 and 40 cm²/Vs, revealed relatively high charge-carrier mobilities, which had a significant impact on the PCE of perovskite solar cells. Large polaron transport was the primary transport mechanism in lead-halide perovskites. Large polaron transport and alloy scattering were the two fundamental processes in lead mixed-halide perovskites. This work advances our knowledge of the transport mechanisms in MHPs and paves the way for the development of novel perovskite materials for solar energy conversion.

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Table 1. Constant parameters used in the mobility calculations at 300 K (m_0 is the free electron mass).

Material	m_e^*/m_0	m_h^*/m_0	ϵ_∞	ϵ_0	$\hbar\omega_{LO}$ (meV)	a (Å)
Lead halide ^{9,11}						
MAPbI ₃	0.21	0.28	5.4	30.4	11.5	
FAPbI ₃	0.22	0.27	5.5	45.0	11.5	
FAPbBr ₃	0.35	0.40	4.5	43.0	16.5	
FA _{0.83} CS _{0.17} PbI ₃	0.22	0.27	5.5	45.0	15.0	
FA _{0.83} CS _{0.17} PbBr ₃	0.35	0.40	4.5	43.0	15.0	
Lead mixed halide ¹¹						
FA _{0.83} CS _{0.17} Pb(I _{0.7} Br _{0.3}) ₃	0.22	0.27	5.5	45.0	13.0	6.202
FA _{0.83} CS _{0.17} Pb(I _{0.6} Br _{0.4}) ₃	0.27	0.35	5.5	45.0	13.0	6.200
FA _{0.83} CS _{0.17} Pb(I _{0.5} Br _{0.5}) ₃	0.27	0.35	5.5	45.0	13.0	6.144
FA _{0.83} CS _{0.17} Pb(I _{0.4} Br _{0.6}) ₃	0.35	0.40	5.5	45.0	13.0	6.072
FA _{0.83} CS _{0.17} Pb(I _{0.3} Br _{0.7}) ₃	0.35	0.40	5.5	45.0	13.0	6.041

Table 2. Calculated coupling constants, RT mobilities, and experimental data in lead halides.⁵⁻⁷

Material	α_e	α_h	$\mu_{LP,e}$ (cm ² /Vs)	$\mu_{LP,h}$ (cm ² /Vs)	$\Sigma \mu$ (cm ² /Vs)	Experiment $\phi \Sigma \mu$ (cm ² /Vs)
MAPbI ₃	2.39	2.76	20.5	11.7	32.2	35 ⁵
FAPbI ₃	2.57	2.85	17.1	11.4	28.5	27 ⁶
FAPbBr ₃	3.37	3.61	7.0	5.3	12.3	14 ⁶
FA _{0.83} CS _{0.17} PbI ₃	2.25	2.49	23.5	15.9	39.4	40 ⁷
FA _{0.83} CS _{0.17} PbBr ₃	3.54	3.78	6.0	4.6	10.6	10 ⁷

Table 3. Calculated coupling constants, RT mobilities, and experimental data in lead mixed-halides.⁷

Material	α_e	α_h	$(\mu_{LP,e}^{-1} + \mu_{AL,e}^{-1})^{-1}$ (cm ² /Vs)	$(\mu_{LP,h}^{-1} + \mu_{AL,h}^{-1})^{-1}$ (cm ² /Vs)	$\Sigma \mu$ (cm ² /Vs)	Experiment $\phi \Sigma \mu$ (cm ² /Vs)
FA _{0.83} CS _{0.17} Pb(I _{0.7} Br _{0.3}) ₃	2.41	2.68	16.6	10.8	27.4	24 ⁷
FA _{0.83} CS _{0.17} Pb(I _{0.6} Br _{0.4}) ₃	2.68	3.05	10.6	6.1	16.7	19 ⁷
FA _{0.83} CS _{0.17} Pb(I _{0.5} Br _{0.5}) ₃	2.68	3.05	10.5	6.1	16.6	15 ⁷
FA _{0.83} CS _{0.17} Pb(I _{0.4} Br _{0.6}) ₃	3.05	3.26	6.2	4.8	11.0	13 ⁷
FA _{0.83} CS _{0.17} Pb(I _{0.3} Br _{0.7}) ₃	3.05	3.26	6.5	4.8	11.3	12 ⁷

Table 4. Calculated polaron binding energies (E_P) and large polaron radii (L_P) in MHPs.

Material	$E_{P,e}$ (meV)	$E_{P,h}$ (meV)	$L_{P,e}$ (Å)	$L_{P,h}$ (Å)
Lead halide				
MAPbI ₃	7.0	9.3	40.0	34.0
FAPbI ₃	8.0	9.9	39.0	35.0
FAPbBr ₃	19.8	22.8	26.0	24.0
FA _{0.83} CS _{0.17} PbI ₃	8.0	9.8	34.0	31.0
FA _{0.83} CS _{0.17} PbBr ₃	20.0	22.7	27.0	25.0
Lead mixed halide				
FA _{0.83} CS _{0.17} Pb(I _{0.7} Br _{0.3}) ₃	8.0	9.9	36.0	33.0
FA _{0.83} CS _{0.17} Pb(I _{0.6} Br _{0.4}) ₃	10.0	12.8	33.0	29.0
FA _{0.83} CS _{0.17} Pb(I _{0.5} Br _{0.5}) ₃	10.0	12.8	33.0	29.0
FA _{0.83} CS _{0.17} Pb(I _{0.4} Br _{0.6}) ₃	12.8	14.6	29.0	27.0
FA _{0.83} CS _{0.17} Pb(I _{0.3} Br _{0.7}) ₃	12.8	14.6	29.0	27.0

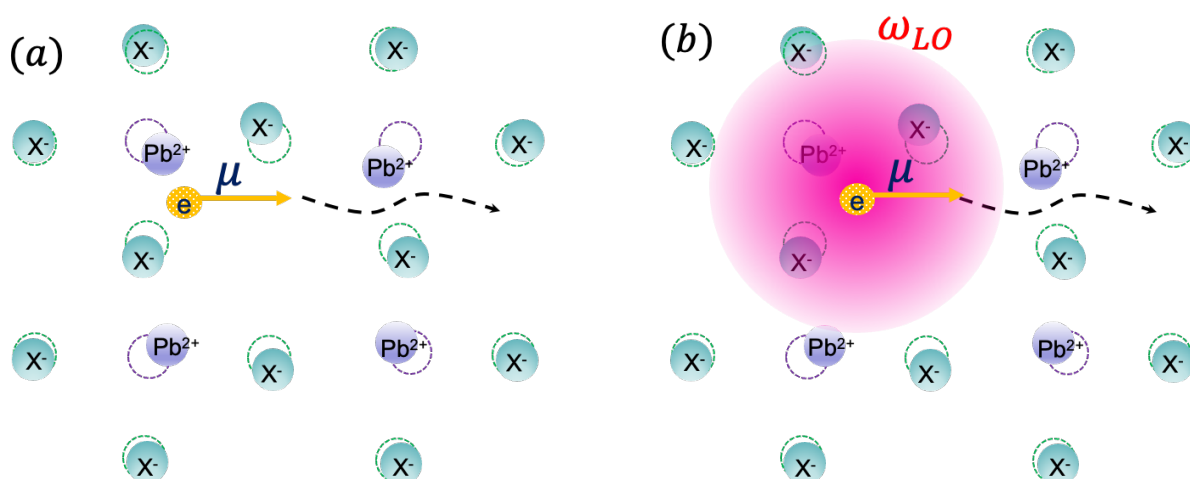


Figure 1. The large polaron transport model. (a) Ionic crystal polarization results from lattice distortion that occurs when an electron travels in a polar lattice and follows its path. (b) A large electron polaron is a dressed particle produced by an electron coupled with an LO phonon cloud created from self-induced polarization (pink circle), and the polaronic effect shows the defect tolerance attained through atomic screening.

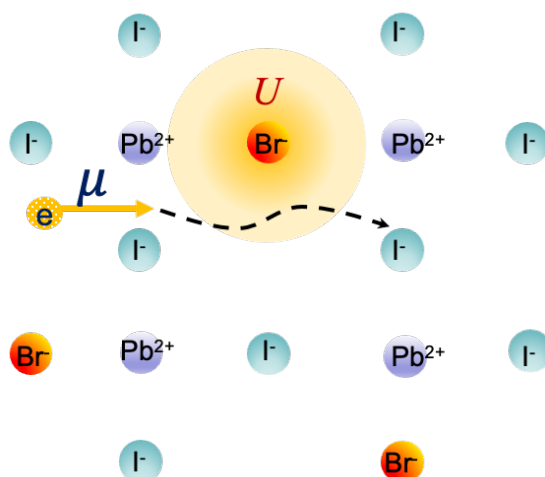


Figure 2. The alloy scattering model. The yellow circle represents the alloy scattering potential (U), which is the scattering source resulting from a random distribution of Br⁻ atoms in the initial I⁻ sites of lead mixed halides.

Synthesis of Graphene from Agricultural Waste for Electrodes in Capacitive Deionization Applications

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Abstract:

In this study, reduced graphene oxide was synthesized from sugarcane bagasse (SB) to use as electrodes in capacitive deionization. SB was converted to biochar by dehydration reaction with concentrated H₂SO₄. Then biochar was converted to graphene oxide (GO) by H₃PO₄-assisted Hummers' method. Finally, GO was reduced by ascorbic acid solution, giving reduced graphene oxide (rGO). Fourier-transform infrared (FTIR) spectrum of biochar compared to SB showed decrease in peak intensity at 1033 cm⁻¹ (C-O stretching) and 3350 cm⁻¹ (O-H stretching) and increase in peak intensity at 1423 cm⁻¹ (C-C stretching) and 1597 cm⁻¹ (C=C stretching), suggesting the conversion of lignocellulose into graphitic structure. This agrees with Raman spectra which showed D band at around 1340 cm⁻¹ and G band at around 1580 cm⁻¹ which belong to graphitic carbon. For GO, FTIR spectrum showed increase in peak intensity at 1032-1080 cm⁻¹ (C-O stretching) and 1189 cm⁻¹ (C-H wagging), suggesting the oxidation of biochar and the presence of functional groups with O and H. On the other hand, FTIR spectrum for rGO showed the opposite change, suggesting the reduction of GO and partial removal of functional groups with O and H from GO. These suggest that SB was successfully converted to rGO.

1. Introduction

Capacitive deionization (CDI) has received increasing interest as a solution for freshwater shortage because of its low energy requirement and lower cost compared to other methods. In CDI technique, two electrodes are oppositely biased so that Na⁺ and Cl⁻ ions are moved to each electrode by Coulomb force and then absorb at surface of electrodes. Carbon materials are considered as one of the promising candidates for electrodes in CDI because of their large surface area, high conductivity and high chemical stability, but CDI performance may be limited by their hydrophobicity. In this study, reduced graphene oxide (rGO) is focused on because its hydrophilic surface, in addition to large surface area and low electrical resistance. It is expected to give increased salt absorption capacity compared to other type of carbon electrodes.¹⁻⁴ Conventionally, rGO is synthesized by reducing graphene oxide (GO) obtained from Hummers' method, using graphite as starting material. In this study we used biochar derived from sugarcane bagasse (SB) through dehydration reaction with concentrated H₂SO₄, as starting material for Hummers' method because this can lower the cost

and can offer a possibility for up cycling agricultural waste.

In this study, during biochar synthesis, the weight-to-volume ratio between SB and concentrated H₂SO₄ were varied. The obtained biochar was then oxidized into graphene oxide by improved Hummer's method⁵ and then reduced by ascorbic acid solution. The physicochemical properties of the product from each step were investigated by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy.

2. Materials and Methods

2.1 Materials

Sugarcane bagasse was obtained from Kaset Phol sugar Ltd., Udon Thani, Thailand. H₂SO₄ 96% (Carlo Erba reagents), H₃PO₄ 85% (Merck) KMnO₄ (Carlo Erba reagents), H₂O₂ 40% (Carlo Erba reagents), HCl 37% (Qrec), Ascorbic acid (Carlo Erba reagents) and NH₃ solution 25% (Qrec) were used in biochar, GO and rGO synthesis. N-methyl-pyrrolidone (Qrec), Polyvinylidene fluoride (MTI) were used in CDI electrode fabrication.

2.2 Methods

SB was washed by deionized water (DI water) and dried in sunlight. After that it was

ground into powder and was heated in oven at 80°C for 12 hours to drive away remaining moisture. Then the powder was sieved through 250 mesh to obtain fine powder.

In dehydration process, 2 g, 2.5 g, 3 g, and 3.5 g of SB were separately mixed with 10 mL of concentrated H₂SO₄ for 10 minutes (Hereafter referred to as B2.0, B2.5, B3.0, B3.5, respectively). After reaction was finished, the obtained biochar was washed by DI water and filtered by vacuum.

For improved Hummers' process, 1 g of biochar was added into a mixture consisting of 54 mL of concentrated H₂SO₄ and 6 mL of H₃PO₄ (80%) in ice bath. Then 3.5 g of KMnO₄ was slowly added while stirring. The slurry was then stirred at 35 °C for 3 hours. After that 46 mL of DI water was added and stirred for 15 minutes. Then 100 mL of DI water is added and the reaction was terminated by adding a small amount of H₂O₂. The slurry was mixed with 5% HCl solution and then washed by DI water and filtered by vacuum to obtain the powder (denoted as GO).

For reduction of GO, GO powder was added into NH₃ solution where pH of 10 was maintained. Then 1 g of ascorbic acid was added to reduce GO. Lastly, the product was dried at 50 °C for 24 hours in oven (denoted as rGO).

CDI electrodes were fabricated by mixing commercial rGO with carbon black, N- methylpyrrolidone (NMP) and Polyvinylidene fluoride (PVDF). The mixture was then coated on Cu sheet. CDI electrodes were attached to current collector (Ti sheet), as shown figure 1. NaCl solution was fed through peristaltic pump and conductivity of solution was measured at out flow. During CDI,

applied electrical bias was varied and initial concentration of NaCl solution was 100 mg/L.

2.3 Characterization

SB, biochar from each condition, GO and rGO were characterized by Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy using 532 nm laser for excitation. In CDI, the concentration of NaCl solution was measured by conductivity meter. Conductivity of NaCl solution with known concentrations was first measured, in order to create detection line, to be used in NaCl concentration monitoring during CDI. Electrosorption capacity for each applied electrical bias was calculated from

$$\frac{C_0 - C_t}{m} V$$

Here, C_0 , C_t are initial and final NaCl concentration, respectively. V is volume of solution and m is mass of electrodes.

3. Results and Discussion

3.1 Biochar Synthesis by Dehydration

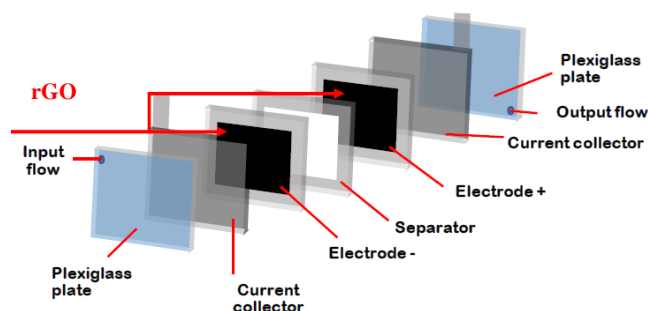


Figure 1 Schematic of CDI cell.

Conditions Sugar cane bagasse (g) : H ₂ SO ₄ (ml)	0s	10s	20s	30s	60s	120s	% yield
2.0:10 (B2.0)							51.1 - 52.1
2.5:10 (B2.5)							53.9 - 54.5
3.0:10 (B3.0)							51.6 - 55.4
3.5:10 (B3.5)							55.3 - 55.9

Figure 2 Dehydration reaction of SB and product yield for each SB: H₂SO₄ condition.

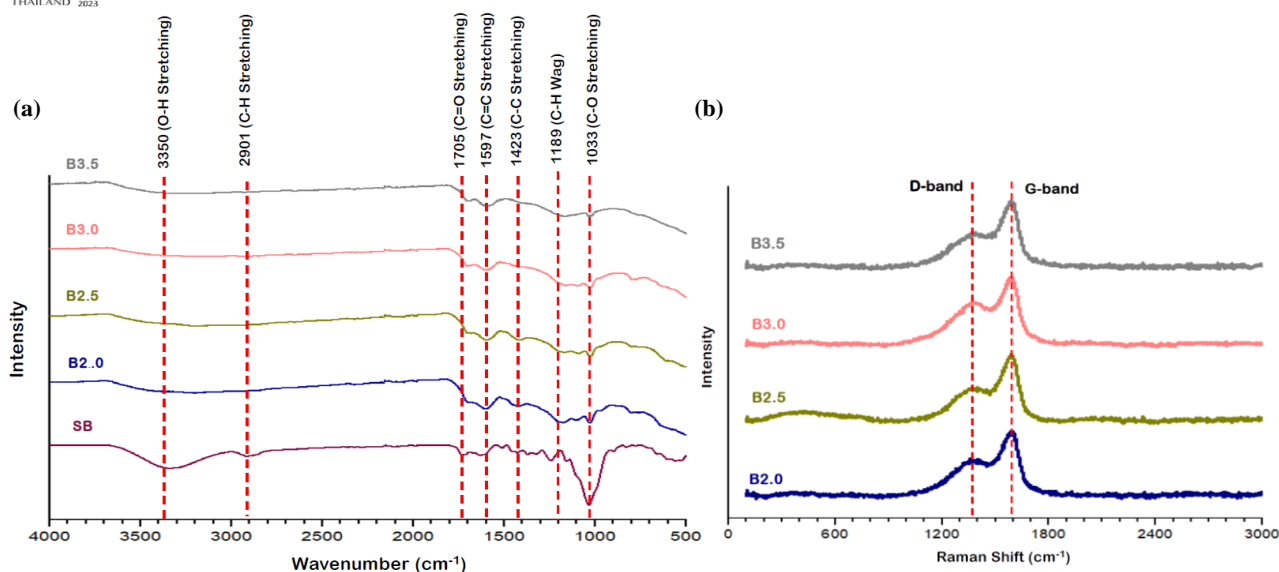


Figure 3 (a) FTIR spectra of SB and biochar from each SB: H₂SO₄ condition. (b) Raman spectra of biochar from each SB: H₂SO₄ condition.

Figure 2 shows the dehydration reaction and product yield which is fraction of weight of obtained biochar compared to weight of sugarcane bagasse used in reaction for each ratio between SB and concentrated H₂SO₄. It can be seen that all conditions underwent complete reaction and B3.5 gave highest product yield for BC. FTIR spectra for SB and biochar obtained from each condition are shown in figure 3 (a). It can be seen that spectra of all biochar showed decrease in peak intensity at 1033 cm⁻¹ (C-O stretching) and 3350 cm⁻¹ (O-H stretching) and increase in peak intensity at 1423 cm⁻¹ (C-C stretching) and 1597 cm⁻¹ (C=C stretching), compared to SB, suggesting that lignocellulose was converted into graphitic structure through dehydration reaction with

concentrated H₂SO₄. Figure 3 (b) shows Raman spectra for biochar obtained from each condition. All conditions show D band at around 1340 cm⁻¹ and G band at around 1580 cm⁻¹ which belong to graphitic carbon, in agreement with FTIR spectra. B3.5 shows highest ratio between intensity of G band to D band (I_G/I_D), in addition to highest product yield. Therefore, biochar obtained from this condition was selected as starting material for GO and rGO synthesis.

3.2 GO and rGO synthesis

Figure 4 shows FTIR and Raman spectra of BC, GO and rGO obtained from B3.5 condition. FTIR spectrum of GO shows increase in peak

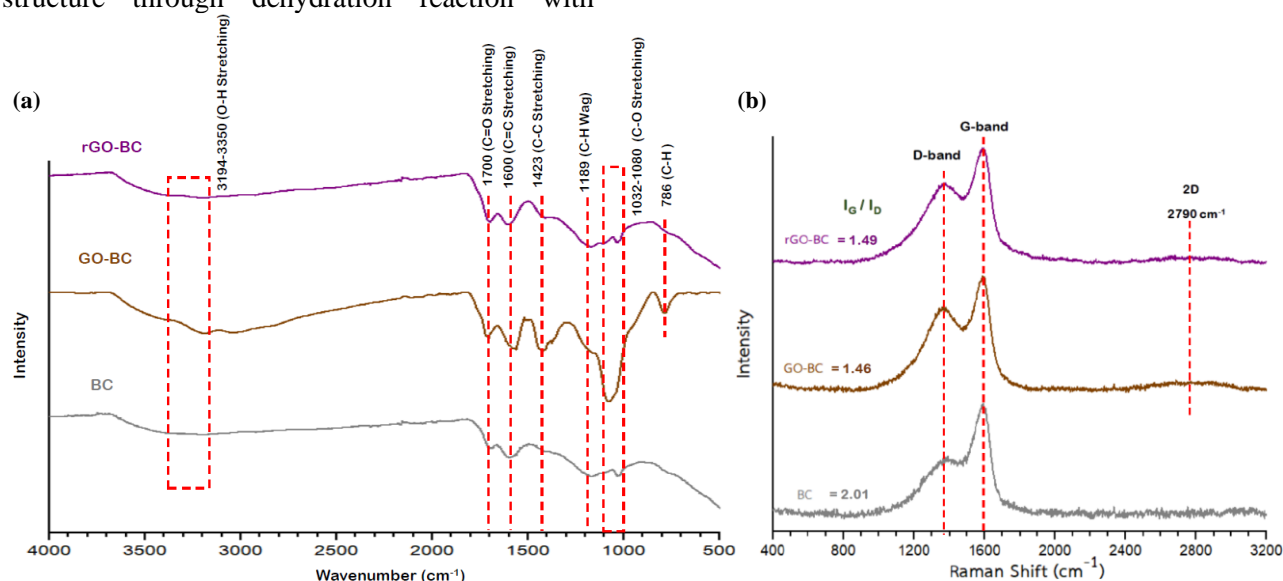


Figure 4 (a) FTIR spectra of BC, GO and rGO. (b) Raman spectra of BC, GO and rGO

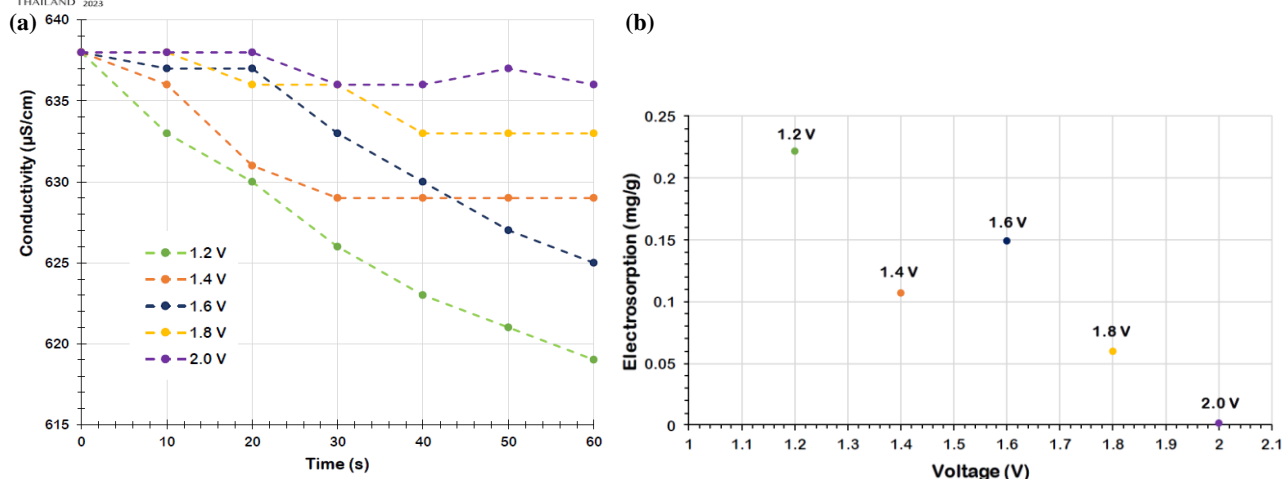


Figure 5 CDI (a) Conductivity of NaCl solution during CDI operation for each applied electrical bias. (b) Electrosorption capacity for each applied electrical bias.

intensity at 1032-1080 cm^{-1} (C-O stretching) and 1189 cm^{-1} (C-H wagging), compared to BC, suggesting the oxidation of BC and the presence of functional groups with O and H. Raman spectrum of GO shows increase in D band intensity compared to G band, resulting in smaller I_G/I_D , suggesting increase in number of defects, which could be the result of oxidation. For rGO, FTIR spectrum shows decrease in peak intensity at 1032-1080 cm^{-1} (C-O stretching) and 1189 cm^{-1} (C-H wagging) compared to GO, suggesting the reduction of GO and partial removal of functional groups with O and H from GO. Raman spectrum of rGO shows no significant change in D band intensity compared to G band. This could be because the removed functional groups with O and H from GO did not recover hexagonal structure of graphene honeycomb, only left defect sites in the structure. Also, in GO and rGO very broad Raman peak around 2790 cm^{-1} was observed. This resembles 2D band of graphene, implying the increase in periodicity of structure.

3.3 Capacitive Deionization

Figure 5 (a) shows change in conductivity during CDI. Bias of 1.2 V showed the largest decrease in conductivity, compared to other larger bias. This could be because of contribution from electrolysis of water or electrochemical reaction with Cu sheet at higher bias voltage, tampering with overall ion concentration. The electrosorption over operation time for 1.2 V was calculated to be 0.22 mg/g. Further improvement in stability over longer operation time is needed.

Conclusion

SB was successfully converted into biochar through dehydration reaction with concentrated H_2SO_4 , as seen from FTIR spectra where peak intensity of C-O stretching and O-H stretching was decreased, but peak intensity of C-C stretching and C=C stretching increased. D band and g band of graphitic carbon was observed in Raman spectrum, indicating carbonization of SB. Weight-to-volume ratio between SB and concentrated H_2SO_4 of 3.5 g: 10 mL gave the highest product yield and highest I_G/I_D . GO was successfully synthesized from biochar, as shown by FTIR spectrum where peak intensity of C-O stretching and C-H wagging increased and by Raman spectrum where I_G/I_D decreased. GO was reduced in rGO as shown by FTIR spectrum where peak intensity of C-O stretching and C-H wagging decreased. CDI operation using rGO as electrode was confirmed, with electrical bias of 1.2 V giving highest electrosorption capacity compared to other voltages.

Acknowledgements

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Synthesis and Characterization of Mixed-Metal Azolate Frameworks via Post-Synthetic Process

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Abstract:

A mixed-metal approach is a useful strategy for achieving a variety of desired properties or functionalities in metal-organic frameworks (MOFs) that may not be available in a single-metal system. This method involves incorporating two or more different metal ions into the framework structure. In this study, we synthesized mixed-metal azolate frameworks and conducted a comparative analysis of their properties in relation to those of single-metal MOFs. Mixed-metal Cu/Ni-triazole was obtained through a post-synthetic metal-exchange reaction, preserving the structure and morphology of the original Cu-triazole framework.

1. Introduction

Metal-organic frameworks (MOFs) are a class of crystalline porous materials that constructed from metal ions or cluster coordinated with organic ligand. This material has attracted much attention owing to their high surface area, tunable pore size, and rational design. MOFs are being extensively explored as potential materials for various applications, including gas storage¹ and separation², drug delivery³, chemical sensors⁴, and catalysis⁵. Various synthetic approaches have been employed to achieve specific properties for particular applications. One interesting approach is the use of mixed-metal MOFs, which incorporates two or more different metal ions into their structure, providing options for multifunctionality and tailoring material properties to a given application. In many cases, due to the synergistic effects derived from the presence of multiple metals, mixed-metal MOFs demonstrate superior performance across a wide array of applications compared to their single-metal counterparts^{6,7}. Mixed-metal MOFs can be obtained through either one-pot synthesis or post-synthesis modifications. In this study, post-synthetic metal exchange process was employed. This method has been often used when the metals possess significantly reactivity in the formation for framework resulting in the difficulty in the direct one-pot synthesis. In metal exchange process, the parent MOF is added to a system with the presence of the second metal solution and then allows the exchange proceed. $[M_3(trz)(\mu_3-OH)]X_2 \cdot 6H_2O$ ($M = Cu$ or Ni , $X = Cl$ and $trz = triazolate$), namely M - trz , represents an intriguing MOF with numerous potential applications^{8,9}. The three-dimensional framework of M - trz is constructed by secondary building

unit (SBU) of $M_3(trz)_3(\mu_3-OH)$, formed by three triazole linkers coordinated with three metal ions in a triangular arrangement. These metal ions within the unit are interconnected by an oxygen atom positioned at the center of the triangle, as shown in Figure 1. The framework can be constructed from either Cu or Ni metals, resulting in Cu- trz and Ni- trz , respectively. Even though they share the same structure, their properties are distinctive depending on the metal center. Cu-MOF, facily obtained by mixing of $CuCl_2$ and trz in DI-water at room temperature, demonstrates poor thermal stability¹⁰. The framework collapses at approximately 225°C, as indicated by thermogravimetric analysis (TGA) results. On the other hand, Ni- trz displays much higher thermal stability (up to 400 °C). Its robustness is beneficial for various applications, especially catalysis. However, its synthesis involves complex procedures, including the use of hazardous hydrofluoric acid (HF), under high synthetic temperatures (200°C), for 48 hours. This limitation hinders the scale-up process to realize practical applications¹¹.

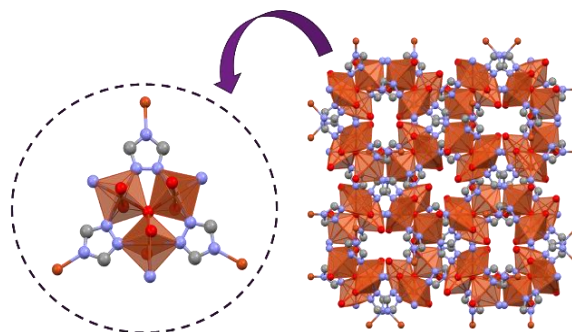


Figure 1. Triangular metal cluster and M - trz framework

In this study, we successfully obtained a mixed metal framework, Cu/Ni-trz, through the metal exchange process. Cu ions in the parent Cu-trz framework were partially replaced by Ni ions using the microwave-assisted hydrothermal method. The structural integrity and morphology of the resulting mixed metal framework were maintained. Additionally, the thermal stability of the framework increased by 15°C after the incorporation of Ni ions in the structure, opening up opportunities for further applications^{12, 13}.

2. Materials and Methods

2.1 Materials

Copper chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Supelco, $\geq 99.0\%$), 1,2,4-triazole (TCI, $> 99.0\%$), Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Supelco $\geq 98.0\%$), Nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 98.0\%$), Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 97.0\%$) were used without further purification.

2.2 Synthesis

Preparation of Cu-trz

Cu-trz was synthesized following the previously reported protocol¹⁰. In general, 1,2,4-triazole (0.14 g, 2 mmol) was dissolved in 10 ml deionized water. Then, the solution was added into 50 ml of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (0.34 g, 2 mmol) at room temperature under stirring 30 m, obtaining the blue powder product.

Preparation of Cu/Ni-trz

Cu/Ni-trz was synthesized by post-synthetic metal exchange process. The powder of synthesized Cu-trz (100 mg) was added to Ni salt solutions (4 mmol in 10 ml). The resulting mixture was heated using microwave radiation (CEM Discovery). Subsequently, the product was washed multiple times with deionized water (DI) and dried at 50°C for 24 hours in a vacuum oven.

The names of each sample indicated in this study correspond to post-synthesis condition. For instance, Cu/ NiCl_2 -trz 200°C 30m refers to Cu-trz with post-synthesis Ni exchange using NiCl_2 as a Ni salt at 200°C for 30 min.

2.3 Characterization

Crystalline phase identification was performed using powder X-ray diffractometer (PXRD, Bruker, New D8 advance, $\text{Cu K}\alpha$, $\lambda = 1.5406 \text{ \AA}$). Product morphology and element analysis were examined by a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-7610F) equipped with energy dispersive spectroscopy

(EDS, Oxford X-max 150 mm²) operating in a gentle beam mode (0.5-2.0 kV). Particle sizes of the obtained samples were calculated by ImageJ software. Before measurement, the samples were spluttered with platinum at 10 mA for 60 sec to increase the surface conductivity. Thermogravimetric analysis (TGA) measurements were performed on Rigaku thermal plus evo2 (TG 8121) under nitrogen atmosphere with the flow rate of 200 cm³ min⁻¹ and the ramping rate of 5°C min⁻¹.

3. Results

3.1 XRD

Figure 2. shows the XRD patterns of as-synthesized Cu-trz and prepared Cu/Ni-trz samples. The peak pattern of Cu-trz is consistency with the simulated pattern according to the reported data¹⁰, confirming the successful synthesis of Cu-trz parent framework. Also, the XRD patterns of the mixed metal Cu/Ni-trz obtained through various methods match well with the characteristic peaks of Cu-trz, suggesting the stable MOF structure after modification. The incorporation of Ni into the framework does not disrupt the structure of the parent Cu-trz during the metal exchange process.

3.2 SEM and SEM/EDS

The morphologies of all samples were confirmed by SEM images as shown in Figure 3a-h. As depicted, the Cu-trz displayed a regular hexagonal shape with an average size of approximately $336 \pm 40 \text{ nm}$ (Figure 3a.). After Ni substitution in the Cu framework, Cu/Ni-trz maintained a regular hexagonal shape with nearly identical particle sizes (Figure 3b-f.), except for Cu/ NiCl_2 -trz 200°C 30m

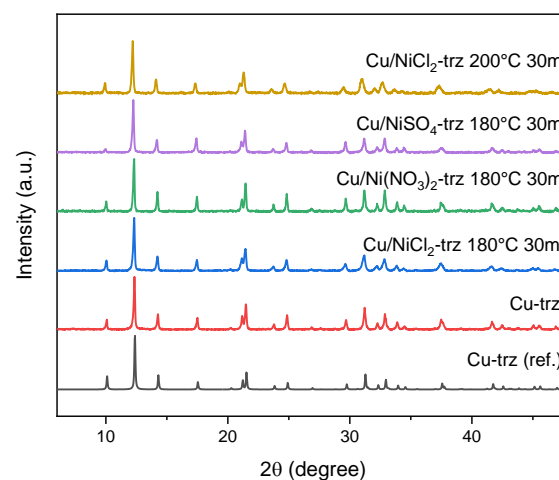


Figure 2. XRD patterns of MOFs.

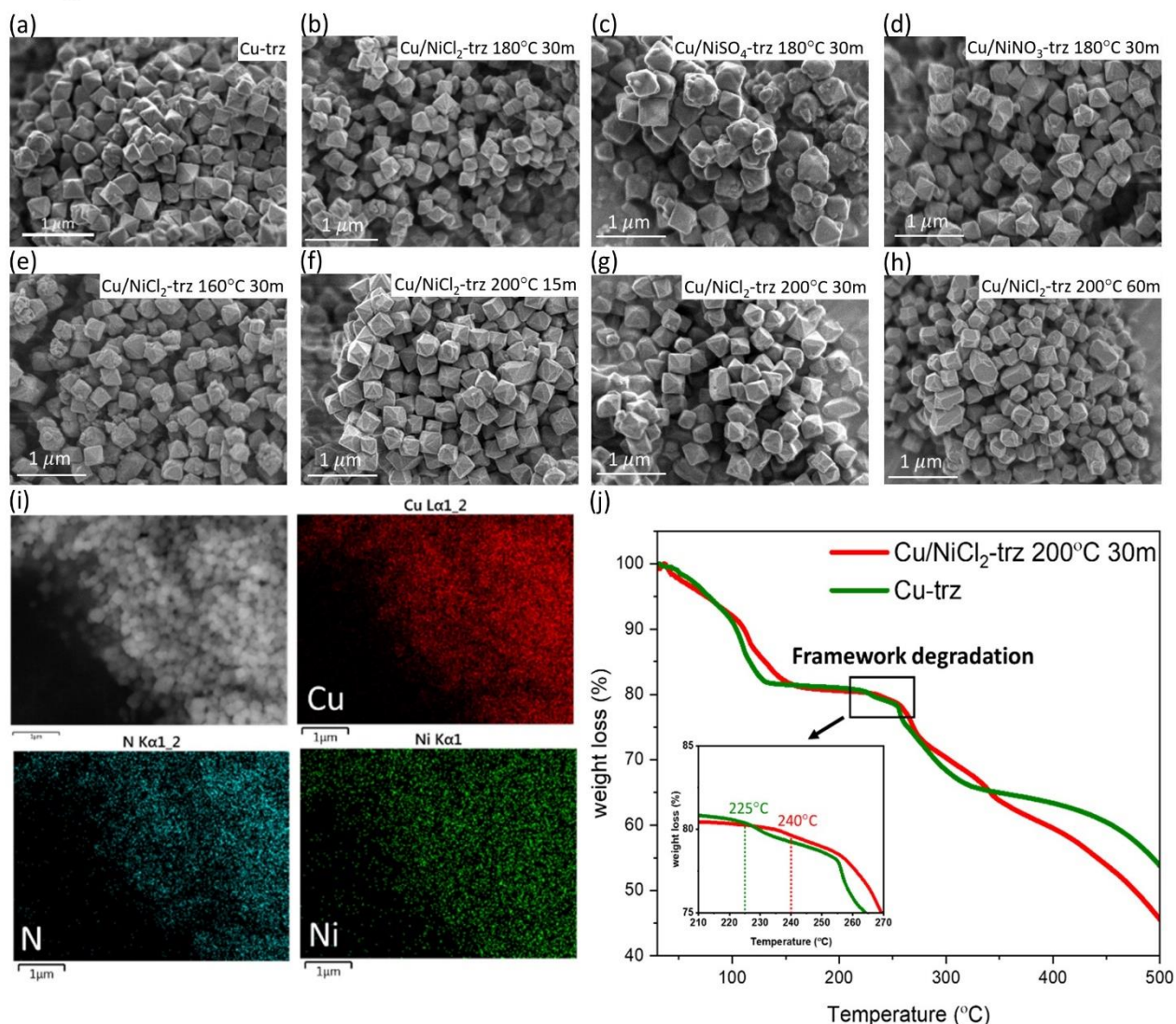


Figure 3. (a-h) SEM images of Cu-trz and Cu/Ni-trz by various metal exchange conditions, (i) SEM/EDS mappings of Cu/NiCl₂-trz 200°C 30m, and (j) TGA plots of MOFs at ramping rate of 5 °C min⁻¹

and 60m which showed a decrease in particle size to 258 ± 40 nm (Figure 3g-h.). The decrease of particle size can be ascribed to the dissolution-recrystallization process induced by the elevated reaction temperatures and prolonged reaction time during the process. The Ni and Cu metal contents in each sample were examined by SEM/EDS, and the results are summarized in Table 1. Varying the Ni salts, NiCl₂ (17.42 % atomic weight) substituted into the framework more effectively than NiSO₄ (11.11 % atomic weight) and Ni(NO₃)₂ (7.03 % atomic weight). This difference is probably due to the varying pH of the resulting solution. Consequently, NiCl₂ was selected as Ni salt for further optimization of synthetic conditions. The reaction temperature was subsequently adjusted, revealing that higher temperatures resulted in

better substitution. Specifically, at 160, 180, and 200°C, the incorporation of Ni into the framework was 12.00, 17.42, and 22.68 % atomic weight, respectively. Finally, the reaction time was optimized using NiCl₂ and 200°C conditions. Reaction times of 15, 30 and 60 min produce the mixed metal framework with rather similar Ni contents of 20.58, 22.68, and 23.58 % atomic weight, respectively. It was found that the reaction time does not severely affect the substitution process of Ni. We further analyze the distribution of Ni in the mixed-metal framework. Figure 3i. reveals the homogeneous distribution of Ni in the framework of Cu/NiCl₂-trz 200°C 30m. This suggests the homogeneous substitution of the Ni inside the framework for every mixed-metal samples.

Table 1 The metal content in Cu/Ni-trz MOFs with various parameters of metal exchange process

Parameter	Condition	Ni (% atomic weight)	Cu (% atomic weight)
Ni salts	NiCl ₂ ·6H ₂ O ^a	17.42	82.58
	NiSO ₄ ·6H ₂ O ^a	11.11	88.89
	Ni(NO ₃) ₂ ·6H ₂ O ^a	7.03	92.97
Temperature	160°C ^b	12.00	88.00
	180°C ^b	17.42	82.58
	200°C ^b	22.68	77.32
Time	15m ^c	20.58	79.42
	30m ^c	22.68	77.32
	60m ^c	23.58	76.42

Post-synthesis condition, a; 180°C for 30m, b; using NiCl₂·6H₂O as Ni salt for 30m, and c; using NiCl₂·6H₂O as Ni salt at 200°C

3.3 TGA

The thermal stability of the MOFs was determined through TGA, and the results are depicted in Figure 3j. Cu/NiCl₂-trz 200°C 30m was chosen as a representative of the mixed metal structure due to its high content of Ni ions. Below 100°C, a drop in the TGA profiles of both Cu-trz and Cu/Ni-trz was observed, attributed to the loss of water solvent, suggesting the porous structure of both frameworks. The facilely synthesized Cu-trz exhibited framework thermal degradation around 225°C. In contrast, the mixed metal Cu/NiCl₂-trz 200°C 30m displayed higher framework thermal stability, collapsing at approximately 240°C – 15°C more stable than Cu-trz. These results indicate that the substitution of Ni in the MOF can improve the thermal stability of a mixed-metal MOF.

Conclusion

This work demonstrates post-synthesis Ni exchange on Cu-trz using the microwave-assisted hydrothermal method. This process resulted in the formation of Cu/Ni-trz, which maintained its crystalline structure and exhibited a uniform distribution of Ni within the Cu/Ni-MOF. Importantly, the incorporation of Ni led to an enhancement in the thermal stability of the mixed-metal MOF. We anticipate that this achievement will pave the way for the utilization of the mixed-metal Cu/Ni-trz MOF in various applications.

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Tailoring Structural and Electrochemical Properties by Metal-Ion Tuning of Ni/V Layered Double Hydroxide

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Abstract:

Recently, transition metals layered double hydroxides (LDHs) have been widely used for energy storage applications because of their two-dimensional layered structure, environmentally friendly nature, cost-effectiveness, and excellent electrochemical performance. However, their property of structural tunability by varying metal ion ratios still needs to be explored to investigate the effect on physicochemical and electrochemical properties. Herein, different molar ratios of Ni:V=5:1, 3:1, 1:1, 1:3, and 1:5 were synthesized using hydrothermal process. Ni:V=1:1 showed the highest areal capacitance of 4451 mF cm⁻² at current density of 4 mA cm⁻². Among the Ni- and V-dominant ratios, Ni:V=5:1 showed the highest areal capacitance of 3317 mF cm⁻² while Ni:V=1:3 showed areal capacitance of 2034 mF cm⁻². The cycling stability test confirmed that Ni:V=3:1 and 1:5 showed high capacitance retention of 102% and 56% after 1000 cycles at current density of 15 mA cm⁻². Increasing the Ni ratio in LDH induced higher degree of structural arrangements without hydroxyl group defects resulting in better electrochemical performance in the form of areal capacitance and cycling stability. An increase in V-metal increased the rate performance and showed higher conductivity. Based on the results of varying molar ratios, it was inferred that Ni:V=5:1 and 1:5 were the best-optimized ratios.

1. Introduction

Sustainable, clean, and non-conventional energy storage systems, predominantly batteries and supercapacitors, store energy from renewable energy resources and supply energy to remote areas.¹ For the development of sophisticated and miniaturized supercapacitors and batteries, and to achieve high energy and power densities, the choice of efficient electrode materials has been a topic of interest. Transition metal layered double hydroxides (LDHs) have attained considerable attention for commercial energy storage devices.² LDH compounds have the generic formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{+x}(A^{n-})_{x/n} \cdot yH_2O$, where M^{II} is a divalent metal ion (e.g., Fe²⁺, Ni²⁺, and Zn²⁺) and M^{III} is a trivalent metal ion (e.g., V³⁺, Ga³⁺, Mn³⁺, and Al³⁺). A^{n-} represents interlayer anionic species, such as CO₃²⁻, SO₄²⁻, NO₃⁻, OH⁻, Cl⁻, and F⁻, that exist with neutral H₂O molecules via hydrogen bonding inside the lamellae.³ LDH materials show a unique brucite-like lamellar structure with high capacitance, large surface area, fast redox reactions during charging and discharging, environmental friendliness, and cost-effectiveness.⁴ Some of the

works have been reported related to the synthesis of Ni/V LDH and their heterostructures. For instance, Wang's group synthesized petal-like Ni/V-S LDH with Ni as the dominant dopant.⁵ Zhang et al. fabricated an in-situ Ni-V LDH/rGO heterostructure with Ni²⁺ as the dominant dopant, finding the optimal Ni:V ratio to be 4:1 for heterostructure synthesis with rGO.⁶ Tu et al., fabricated the heterostructure of Ni:V=2:1 with CNTs using the reflux method for advanced asymmetric supercapacitors. Tu et al. reported the synthesis of Ni/V LDH using a hydrothermal process to fabricate heterostructures with V₂CT_x MXene to enhance the electrochemical performance of supercapacitors. Tu et al. synthesized Ni:V=2:1 heterostructures with CNTs via the reflux method for advanced asymmetric supercapacitors. Tu et al. also reported on synthesizing Ni/V LDH using a hydrothermal process, creating heterostructures with V₂CT_x MXene to enhance supercapacitor electrochemical performance.⁷ Pan's group synthesized a Ni/V LDH heterostructure with ZIF-67 through an in-situ self-assembly process for applications in photocatalysis and energy storage.⁸ Despite successful synthesis of Ni/V LDH with Ni²⁺ as the

dominant metal and high specific capacitances in numerous studies, the effect of Ni^{2+} and V^{3+} as dominant dopants and varying metal ion molar ratios on the structural and electrochemical properties of Ni/V LDHs remains unexplored. As a result, the main objective of this study was the structural tuning of Ni/V LDH by varying metal ion ratios for the investigation of molar ratios on their structural and electrochemical properties. Individual metals' unique redox behavior and electronic configurations will influence the physicochemical properties including *d*-spacing, crystal size, and layered morphology. This work provides an insight into the study of effect of Ni and V ratios affecting the structural and electrochemical properties.

To achieve this, a set of samples with molar ratios of was synthesized by a one-step hydrothermal process. Ni-dominant samples showed higher crystallinity compared to V-dominant LDHs owing to the hydroxyl group defects. Electrochemical results from cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) confirmed the effect of tuning of LDHs by metal ions on their electrochemical properties. Among the Ni- and V-dominant ratios, Ni:V=5:1 showed the highest areal capacitance of 3317 mF cm^{-2} while Ni:V=1:3 showed an areal capacitance of 2034 mF cm^{-2} . The cycling stability test confirmed that Ni:V=3:1 and 1:5 showed high capacitance retention of 102% and 56% after 1000 cycles at the current density of 15 mA cm^{-2} .

2. Materials and Methods

2.1 Materials

Nickle chloride (NiCl_2 , 98%, Sigma-Aldrich), vanadium chloride (VCl_3 , 97%, Sigma-Aldrich), potassium hydroxide (KOH, Sigma-Aldrich) pellets, poly(vinylidene fluoride) (PVDF, average MW=534000, Sigma-Aldrich), urea, (99%, Sigma-Aldrich), N-methyl-2-pyrrolidone (NMP, Acros Organics) and conductive carbon (Super P, TIMCAL).

2.2 Synthesis

A one-step hydrothermal process was used to synthesize Ni/V LDH nanosheets by keeping either metal ion as the dominant dopant.⁹ In detail, for the molar ratios of Ni:V=5:1, 3:1, 1:1, 1:3, and 1:5, the amount of each ion was taken in such a way that the final molar ion concentration was retained at 2.4 mmol. In a typical process, x mmol of NiCl_2 ,

and y mmol of VCl_3 were taken along with 0.25 g of urea in 40 ml of DI water and the reaction mixture was magnetically stirred for 1.0 h. Subsequently, the reaction mixture was transferred to a stainless-steel Teflon-lined autoclave vessel and the hydrothermal reaction was performed under sealed conditions at 120°C for 12.0 h. After cooling to room temperature, the precipitates were collected and washed thrice and the product was dried in an oven at 70°C for 12.0 h. The experimental setup is shown in Figure 1.

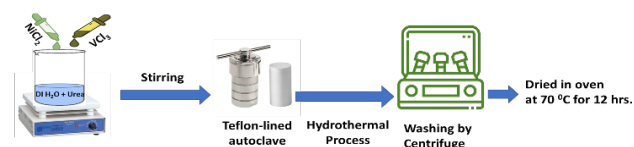


Figure 1. Schematic setup for the synthesis of Ni/V LDHs.

2.3 Characterization

The study of the crystal structure of the as-synthesized Ni/V LDH nanosheets was examined using powder X-ray diffraction (PXRD, D2-Phaser with Cu-K α radiation, $\lambda=0.154 \text{ nm}$). The surface functionality of the materials was studied using Fourier-transform infrared spectroscopy (FTIR, PerkinElmer 2000). The surface morphologies of the samples were examined using field-emission scanning electron microscopy (FE-SEM, HITACHI, SU-80410).

Electrochemical measurements of all LDH samples were performed using a three-electrode cell configuration in a 6 M KOH electrolyte. The working electrode was fabricated by mixing the active material, PVDF, and Super P conductive carbon in the mass ratio of 8:1:1, respectively. Then, the homogenous slurry was coated on a nickel foam current collector followed by hot pressing and dried in an oven at 80°C for 12 h. Cyclic voltammetry analysis at a scan rate of 10 mV s^{-1} , galvanostatic charge-discharge (GCD) at different current densities (4 mA cm^{-2} , 6 mA cm^{-2} , 8 mA cm^{-2} , 10 mA cm^{-2} , 15 mA cm^{-2}), and electrochemical impedance spectroscopy (EIS) analysis in the frequency range of 0.01 Hz–100 kHz was performed. The areal capacitance (F cm^{-2}) was calculated according to the following Equation 1.

$$\text{Areal capacitance} = I \Delta t / \Delta V S \quad (1)$$

where I , $\Delta V \Delta t$, and S are the constant discharge current (A), the potential window (V), the

discharge time (s), and the effective area (cm²), respectively.

3. Results

3.1 Physicochemical Characterization

Figure 2a showed the XRD patterns of the as-synthesized LDH samples with different ratios of Ni:V=5:1, 3:1, 1:1, 1:3, and 1:5. The characteristic peaks located at about 11.5°, 23°, 33.5°, 38.5°, and 60° were most consistent with the distinctive features of carbonate-intercalated layered double hydroxide of Ni and V.¹⁰ XRD pattern of Ni-dominant samples showed high-intensity peaks indicating high crystallinity compared to V-dominant samples. Ni:V=1:1, 3:1, and 5:1 showed large *d*-spacing values including 7.90, 7.82, and 7.74 Å, respectively,

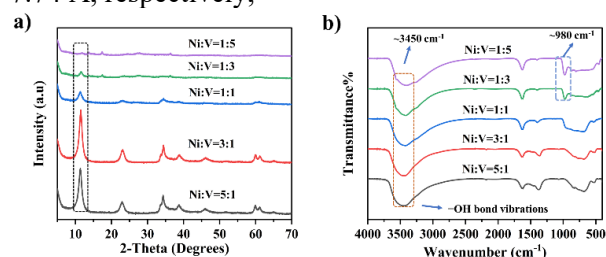


Figure 2. (a) XRD and (b) FTIR spectra of Ni:V=5:1, 3:1, 1:1, 1:3 and 1:5, respectively.

while Ni:V=1:3 and 1:5 showed lower *d*-spacing values of 7.57 and 7.42 Å, respectively as mentioned in Table 1.

Table 1. *d*-spacing and crystallinity values of all samples obtained from XRD data.

Samples	<i>d</i> -spacing <i>d</i> ₀₀₃ [Å]	Crystallinity [%]
Ni:V=5:1	7.74	67.8
Ni:V=3:1	7.82	73.8
Ni:V=1:1	7.90	60.1
Ni:V=1:3	7.57	59.8
Ni:V=1:5	7.42	39.7

The FTIR spectra in Figure 2b corresponded to Ni:V=5:1, 3:1, 1:1, 1:3, and 1:5 respectively. It can be observed that all the samples yielded similar IR spectra. The broad transmission bands at ~3450 cm⁻¹ and 1650 cm⁻¹ for all samples corresponded to the stretching vibrations of the –OH group of hydroxides present on the surface and inside the interlayers of compounds.¹¹ The transmission band at ~1380 cm⁻¹ represented the absorption mode of the interlayer CO₃²⁻ ions.¹² However, for Ni:V=1:3

and 1:5 the shoulder bands at ~980 cm⁻¹ were associated with the stretching vibrational mode of hydroxyl groups from water molecules coordinated with metal ions (Ni²⁺ and V³⁺) that cause the defect resulting in low crystallinity of V-based LDHs. In the low-frequency region of 500–800 cm⁻¹, the transmission bands were related to M–O (Ni–O, V–O) bonds stretching vibrations.¹³

FE-SEM images revealed the surface morphology of Ni:V=5:1, 3:1, 1:1, 1:3, and 1:5. The SEM images are shown in Figures 3a, b, and c for Ni:V=5:1, 3:1, and 1:1 depicted the layered nanoflake structures, respectively.

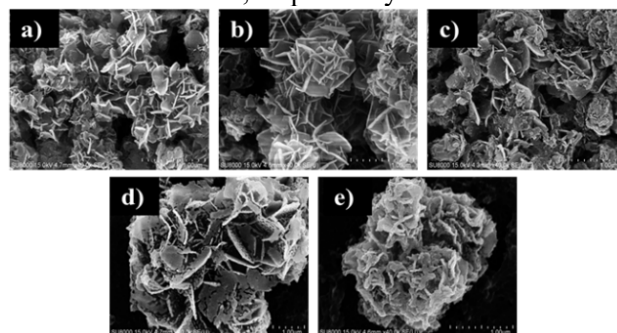
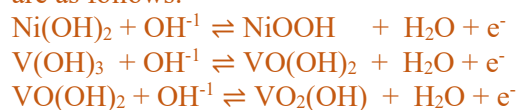


Figure 3. SEM images of (a) Ni:V=5:1 (b) 3:1, (c) 1:1, (d) 1:3, and (e) 1:5.

The SEM images of the Ni:V=1:3 and 1:5 showed accumulated porous and crumpled layered structures with broken edges, as shown in Figures 3d and e, respectively. From the SEM images, the high crystallinity of the Ni-based LDH compounds was more evident than that of the V-dominant compounds, which was also consistent with the XRD results.

3.2 Electrochemical characterization

Cyclic voltammetry (CV) was performed to investigate the electrochemical behavior of Ni:V=5:1, 3:1, 1:1, 1:3, and 1:5 LDH compounds. The CV profile of all samples (as shown in Figure 4a) indicated a redox pair at about 0.36 V and 0.15 V, corresponding to the undergoing redox reactions of Ni and V hydroxides present on the surface of Ni/V LDH. The proposed reversible redox reactions of Ni²⁺/Ni³⁺, V³⁺/V⁴⁺, or V⁴⁺/V⁵⁺ are as follows.



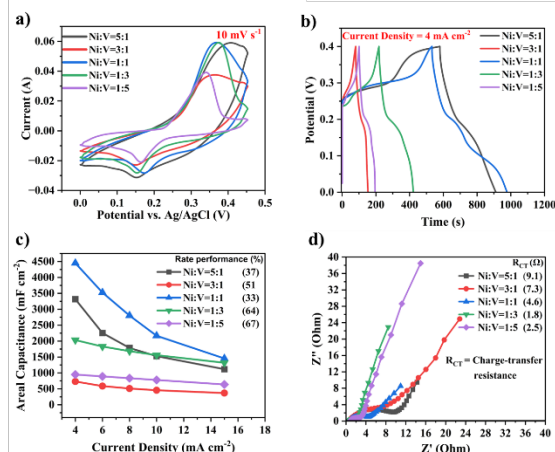


Figure 4. (a) CV and (b) GCD curves of the as-synthesized samples. (c) Capacitance versus current density plot and (d) Nyquist plot before stability test.

The areal capacitance at different current densities and rate performance were obtained from galvanostatic charge-discharge (GCD) analysis (as shown in Figure 4b) performed at different current densities. Ni:V=1:1 exhibited the highest areal capacitance of 4451 mF cm⁻² at the current density of 4 mA cm⁻² while for Ni:V=3:1 and 5:1, the areal capacitance values were calculated as 732.5 mF cm⁻² and 3317 mF cm⁻², respectively. On the other hand, the areal capacitance values for Ni:V=1:3 and 1:5 were found to be 2033 mF cm⁻² and 950.0 mF cm⁻² respectively. Figure 4c shows areal capacitances versus current densities of 4 mA cm⁻², 6 mA cm⁻², 8 mA cm⁻², 10 mA cm⁻², and 15 mA cm⁻². For Ni:V=1:1, the areal capacitance decreased sharply with increase in current densities, whereas for Ni:V=3:1 and 5:1 the decrease in areal capacitance was comparatively slow.

On the other hand, V-dominant samples showed a higher rate performance with the increase in current densities compared to Ni-dominant samples. The rate performance values for all the samples can be seen in Figure 4c. Nyquist plot of all the samples, as given in Figure 4d exhibited that all the samples showed semi-circles in a high-frequency range corresponding to their charge transfer resistance (R_{CT}). Ni:V=1:1, 3:1, and 5:1 showed R_{CT} values of 4.6 Ω, 7.3 Ω, and 9.1 Ω, respectively. Meanwhile, V-dominant samples Ni:V=1:3 and 1:5 exhibited low R_{CT} values of 1.8 Ω and 2.5 Ω, respectively.

Ni:V= 1:1, 1:3, and 1:5 showed poor capacitance retentions of 67%, 43%, and 56%, respectively, while Ni:V=3:1 and 5:1 sample highly retained their capacitances of 102% and 91%, respectively after 1000 cycles as shown in Figure 5a.

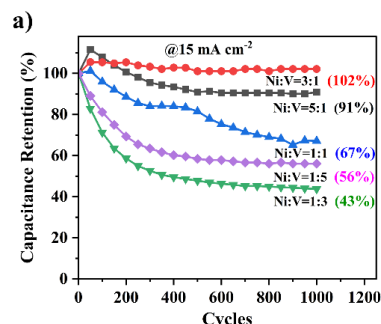


Figure 5. (a) Cycling stability performance of Ni:V=5:1, 3:1, 1:1, 1:3, and 1:5 for 1000 cycles at 15 mA cm⁻².

Conclusion

In summary, the structural tuning of Ni/V LDH was done by varying metal ions and LDH samples were successfully synthesized using a facile one-step hydrothermal process. FTIR results showed the presence of hydroxyl groups for V-dominant LDHs that caused low crystallinity as evident from XRD and SEM results. For electrochemical results, Ni:V=1:1 showed the highest areal capacitance of 4451 mF cm⁻² at the current density of 4 mA cm⁻². For the case of Ni dominance, Ni:V=3:1 and 5:1 showed areal capacitance of 732.5 and 3317 mF cm⁻², respectively. For V-dominance, Ni:V=1:3 and 1:5 showed areal capacitance of 2034 mF cm⁻² and 950.0 mF cm⁻², respectively. The cycling stability test confirmed that Ni:V=3:1 and 5:1 showed high capacitance retention of 102% and 91% after 1000 cycles at a current density of 15 mA cm⁻² whereas, Ni:V=1:3 and 1:5 showed lower capacitance retention of 43% and 56%, respectively. Thus, increasing the Ni ratio in LDH induced a higher degree of structural arrangements without hydroxyl group defects resulting in better electrochemical performance in the form of areal capacitance and cycling stability. The increase in V content decreased the capacitance retention but increased the rate of performance and conductivity. Based on the electrochemical properties it was inferred that Ni:V=5:1, showing high capacitance and cycling stability performance, and Ni:V=1:5 with higher rate performance, and conductivity were the optimized

ratios for further use in various applications. From our standpoint, Ni/V LDH material stands out as an exceptional electrode material, boasting superb structural and electrochemical properties. Nevertheless, to fully comprehend its performance variations across different Ni:V ratios, more in-depth mechanistic studies including comprehensive electronic structure calculations, charge distribution analyses, and spectroscopic investigations are warranted.

Acknowledgments

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The Study of Nanoparticle Composition in Sub-urban area

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Abstract:

Thailand and other Asian countries are currently experiencing growing levels of air pollution. Particles or nanoparticles (NPs) in the atmosphere are an air pollutant that have a harmful impact on human health and the environment when exposed to excessive amounts. Little information is obtained by examining the composition of particles or nanoparticles. Understanding suitable health risk and impact assessment for health risk assessment in acute and chronic effects, as well as including the source of NPs in ambient air, are examples. As a result, this study investigated the chemical composition of NPs (PM_{0.1} and PM_{0.1-0.5}) in rainy season by setting up the NPs sampling for ambient air using cascade air sample for size-classified particle at the rooftop of building of the Robotic Innovation and Automatic Mechanical Center (INNOROBOT), Thailand Institute of Scientific and Technological Research (TISTR), Technotani, Klongluang, Pathumtani province. The samples were collected after 48 hours to determine concentration levels, organic carbon (OC), and elemental carbon (EC) in PM_{0.1}, PM_{0.1-0.5} particle sizes. The average concentration of PM_{0.1} was 9.57 µg/m³, whereas PM_{0.1-0.5} was 14.52 µg/m³. This finding suggested that the average concentration of PM_{0.1} was greater than 50% of the concentration of PM_{0.1-0.5}. When NPs are exposed for an extended period of time, it is probable that they will have a long-term effect on human health. The carbon composition revealed that the average concentration of OC was 0.67 µg/m³, while the average concentration of EC was 0.36 µg/m³, implying that OC was more concentrated than EC. As the composition result of NPs in this study, its emission source can be attributed to diesel exhaust and open biomass burning.

Keywords: Nanoparticle, Chemical Composition, Organic Carbon, Elemental Carbon

1. Introduction

Air pollution has been one of Asia's significant environmental issues in recent decades (Boongla et al., 2019; Tial, 2023; Phairuang et al., 2023). Air pollutants, particularly particulate matter (PM), are produced by both man-made and natural sources, including motor vehicles, households, the industrial sector, agricultural residue burning, and forest fires. Several studies have found that PMs have an impact on human health, urban and rural environments and global climate, either directly or indirectly. Recent studies of ambient PM have revealed that finer particles, particularly nanoparticles (PM_{0.1}), pose a risk to human health (Phairuang et al., 2022). Inhaled nanoparticles may cause lung inflammation and cardiac issues in the body. Breathing in diesel soot creates a general inflammatory response and changes the mechanism that regulates automatic activities in the cardiovascular system, such as heart rate control, according to human studies

(Sonwani et al., 2021). High particle counts, high surface area to mass ratio, oxidative stress potential, high solubility and charge, and facile distal airway penetration characterize combustion particulates containing ultra-fines or PM_{0.1} (PM_{0.1} µm in diameter) (Xuan et al., 2023). South East Asia (SEA) has been a source of PM pollution in the recent decade, affecting countries both inside and outside the region (Boongla et al., 2019). Observations of PM in Thailand and neighboring countries currently is based on the level of coarse and fine particles (Ngoun et al., 2023; Dejchanchaiwong et al., 2020; Choomanee et al., 2020; Hien et al., 2019), and to a lesser extent on sub-micron particles (PM_{1.0}) (Tial et al., 2023; Amin et al., 2023; Vejpongsa et al., 2017) that are observed by both mathematical modeling and actual monitoring on the ground. However, data on the status and properties of ambient PM_{0.1}, as well as its sources, remains scarce. Furthermore, data on the carbon contents of size-specific particles in the small to nano-size range in Asian

countries and Thailand is currently lacking. Only a few studies on nanoparticles and their carbon components have been conducted in Asian countries and Thailand to better understand the levels of air pollution, origins, and effects of nanoparticles (Phairuang et al., 2022). Carbonaceous aerosols (CA) are produced by biomass, coal, and fossil combustion. Open biomass burning is the leading source of black carbon (BC) and organic carbon (OC) in the atmosphere. The term BC, which is roughly equivalent to elemental carbon (EC), is frequently used in climate models to refer to light-absorbing compounds. At the same time, the term EC is preferred in aerosol chemistry areas. CA levels vary according on the source, such as diesel exhaust, coal combustion, and biomass combustion. Furthermore, the features of ambient PM_{0.1} and meteorological influence as a function of season have not been extensively investigated, particularly in Thailand's sub-urban areas.

Pathumtani province is a big city in Thailand, close to the Bangkok Metropolitan Region (BMR). It had a high population density and automobile density, as well as significant economic activity tied to a wide range of enterprises. Several studies, however, defined Pathumtani province as a BMR suburban. This city is quickly expanding, which, like other suburban regions in developing countries in Asia, may contribute to increased air pollution due to its proximity to air pollution emission sources, the objectives of this study were to (1) quantify nanoparticle concentrations; (2) determine the properties of size-fractionated particles bound EC and OC, as well as their correlation; and (3) identify the potential effect of meteorological and these pollutants in the study site. These linkages could help determine the influence of distribution emission.

2. Materials and Methods

2.1 Sampling site

Atmospheric PM was collected with a PM_{0.1} cascade sampler at the rooftop of building of the Robotic Innovation and Automatic Mechanical Center (INNOROBOT), Thailand Institute of Scientific and Technological Research (TISTR), Technotani, Klongluang, Pathumtani province, located in Klong Ha, Klongluang, Pathumtani (Figure 1). The Robotic Innovation and Automatic Mechanical Center at the TISTR is located at

14.044744° (N) and 100.718820° (E). The site is surrounded by rice paddies and fields in which other crops are grown, and there are also some small and medium-sized factories in the area. the INNOROBOT is located close to the northern entrance to TISTR, as shown on the TISTR map, near Phaholyothin Road, a major thoroughfare, so its air quality would be expected to be affected by road transportation, and particularly by the large number of cars and buses that use this road during the rush hour. The total number of vehicles registered in Pathumtani is 151,159 based on 2017 data (Boongla et al., 2019). Pathumtani province is a suburban area inside the BMR in central Thailand. It has a land area of 1,525.860 km² and a population of approximately 1.180247 million as of 2022. It is 27.8 kilometers north of Bangkok's center, and is connected by Paholyothin Road No.1. The yearly average rainfall range is 952-1,125 mm, the average relative humidity (RH) range is 59.0-82.0%, and the average temperature range is 24.0-32.9°C. The coldest month is January, and the hottest month is April (Thailand Meteorological Department, 2019).

2.2 Cascade air sampler for size-classified particles

The ambient aerosol was measured using a cascade air sampler capable of separating particle sizes as small as 100 nm, known as the PM_{0.1} sampler or nanosampler. The cascade impactor is a series of multi-nozzle impactors, used to measure particle mass distribution. Particles were classified into six sizes: <0.1 µm (PM_{0.1}), 0.1-0.5 µm (PM_{0.1-0.5}), 0.5-1.0 µm (PM_{0.5-1}), 1.0-2.5 µm (PM_{1-2.5}), 2.5-10 µm (PM_{2.5-10}), and > 10 µm (PM_{>10}) Phairuang et al. (2022). Each stage was collected using 55-mm quartz fibrous filters (QFF) (Pallflex, 2500 QAT- UP), whereas the IF stage used a stainless-steel filter pack (SUS-316, Fiber Web, Nippon Seisen, fiber diameter = 9.8 m) packed in an initial filter cartridge. An inertial filter with an aerodynamic cutoff diameter of dp50~65 nm. The cascade air sampler was employed at a flowrate of 40 L/min, and 48-hour samples were taken for six consecutive days during the wet season in October 2017. All of the filters were pre-baked for one hour at 350 °C to eliminate any potential contamination before being conditioned in a PM_{2.5} weighing chamber for 48 hours at a relative humidity (RH) of 35±5% and a temperature of 21.5±1.5 °C. In terms of air sampling, the samples were kept at -20

°C in a refrigerator until they were employed in chemical analysis. Blank filters were also utilized to correct for any contamination during filter shipment and sampling. However, during the wet season, the maximum levels of nanoparticles (NPs) are often recorded during the week rather than on weekends.

2.3 Carbonaceous component analysis

The particle-bound carbon components OC and EC were measured using a Laboratory Carbon Aerosol Analyzer using the methodology described by Boongla et al. (2019). Each filter sample had a 1.5 cm² (1.5 cm x 1 cm) portion punched out of it before being placed in a carbon analyzer for examination. The punched filter was heated inside the analyzer at 120, 250, 450, and 550 °C to produce four OC fractions (OC1, OC2, OC3, and OC4) in 100% Helium (He), while the three EC fractions (EC1, EC2, and EC3) were heated at a higher temperature, 550, 700, and 800 °C, respectively, in a mixture of 2% O₂ and 98% He. The data were corrected for the charring of organic materials (OPC) using a reflectance laser. OC and EC values are defined as OC1 + OC2 + OC3 + OC4 + OPC and EC1+EC2+EC3-OPC, respectively.

The char-EC/soot-EC ratios were also calculated, where char-EC equals EC1 minus OPC and soot-EC equals EC2 plus EC3 (Boongla et al., 2019). Carbon assessment quality assurance and control were regulated using a reference standard and blank filters. The carbon analysis was calibrated using total carbon (TC) as measured against sucrose (C₁₂H₂₂O₁₁) as a reference chemical. Based on the measured travel-blank filters (n = 3), the minimum detection limit (MDL) for OC and EC was determined to be 0.2 g/cm² and 0.1 g/cm², respectively. The carbon level in the samples was subtracted from the carbon level in the blank filters.

2.4 Meteorological

During the study period, meteorological data was received from the Meteorology Department of Thailand (TMD), Pathumtani Meteorological Station, Pathumtani Province, relative humidity, temperature, pressure, rainfall, wind speed, wind direction, and possible cover are among the meteorological data. The NPs and meteorological correlation was investigated using the Pearson correlation analysis in SPSS software (version 28). Furthermore, meteorological

conditions have a significant impact on the ambient air quality of metropolitan locations. As a result, the correlations between meteorological and nanoparticle concentrations in Pathumtani, Thailand.

3. Results and Discussion

3.1 Mass concentration of size-fractionated particles

Table 1 shows the size distributions of mass concentrations for atmospheric particles in TISTR, Klong Ha, Pathumtani of Thailand. The highest mass concentration was PM_{2.5-10}, followed by PM_{0.5-1.0}, PM_{>10}, PM_{1.0-2.5}, PM_{0.1}, and PM_{0.1-0.5}, respectively. The average atmospheric PM_{0.1} in TISTR was higher than the corresponding values for Muaro Jambi, Indonesia (9.20 µg/m³) (Amin et al., 2019), while was lower than Pathumtani, Thailand (13.47 µg/m³) (Boongla et al., 2021).

3.2 Size distribution of carbon species

Table 2 shows the carbonaceous components in ultrafine particles (OC, EC, Char-EC, and Soot-EC, and TC) at TISTR, Klong Ha, Pathumtani of Thailand from study period, were measured using the thermal/optical transmittance (TOT) method following the NIOSH870 protocol. The average OC, EC, Char-EC, Soot-EC and TC concentrations and their ratios for PM_{<0.1} in this study are showed in Table 2. This study was investigated carbonaceous aerosols including EC and OC in size-fractionated PM down to PM_{0.1} samples, it is found that OC (0.67 µg/m³) concentrations were higher than EC (0.36 µg/m³) concentrations in study areas (Table 2). Char-EC was 0.12 µg/m³, whereas soot-EC was 0.24 µg/m³ and 1.02 µg/m³ for TC. OC/EC ratios can be used to identify specific sources of carbonaceous particles. The ratios for diesel exhaust, biomass fires, and coal burning varies. The greater ratios are caused by biomass fires, whereas fossil fuel burning results in lower OC/EC ratios (Phairuang et al., 2022; Boongla et al., 2019). This study found that the OC/EC ratio was 1.95.

3.3 Relationship between carbon species

The average OC, EC, TC, char-EC, soot-EC, OC/EC(-) and char-EC/soot-EC concentrations in study period are displayed in Table 2. The char-EC/soot-EC correlation for the PM_{<0.1} at sub-urban area site was less than 1. It suggest a greater influence of diesel exhaust in this

study site. According to Inerb et al. (2022), the Char-EC/Soot-EC ratio is affected by both direct emission sources and moist deposition. Higher Char-EC/Soot-EC ratios suggest that biomass combustion is dominant, as Char-EC contributes to overall EC content. At the same time, ratios less than 1.0 indicate that soot from diesel exhaust makes a considerable contribution to total EC concentrations (Boongla et al., 2022).

The findings of this work is of great importance to air pollutant control policies in sub-urban areas. This study site's source of NPs can be attributed to vehicle emission.

3.4 Correlations between meteorological conditions and $PM_{0.1}$

To find differences among the mass concentrations of mass fractions, the correlations of meteorological factors such as wind speed (Ws), wind direction (Wd), temperature (T), relative humidity (RH), surface pressure (P), and precipitation event (Pr) or rainfall on the mass concentrations of $PM_{0.1}$ also were examined in this study and presented in Table 3 and 4. In Thailand, $PM_{0.1}$ concentrations were highest in the winter and post-monsoon seasons, followed by summer, and

lowest during the monsoon. Our findings of reduced atmospheric particulates concentrations in October are consistent with earlier research (Phairuang et al., 2022; Boongla et al., 2019). The studies focused on the influence of long-range transport of biomass and rice straw burning emissions in Thailand. Wet scavenging of ambient aerosols contributes to frequent precipitation throughout the monsoon season, which lasts from July to October. In addition, $PM_{0.1}$ concentrations were shown to be strongly related to air relative humidity and the number of forest fire hotspots (Sresawasd et al., 2021).

Meteorological conditions in our study revealed that Ws, Wd, and Pr were associated with $PM_{0.1}$, indicating that meteorological conditions influenced $PM_{0.1}$ mass concentration. There is a positive correlation between temperature and $PM_{0.1}$. $PM_{0.1}$ levels increased in tandem with rising temperatures. The negative correlations between relative humidity, pressure, rainfall, wind speed and $PM_{0.1}$ suggest the proportion of the decreasing of $PM_{0.1}$ and the increasing of wind speed. Strong winds generally dilute pollution, therefore, it could eliminate the level of $PM_{0.1}$ in the atmosphere.

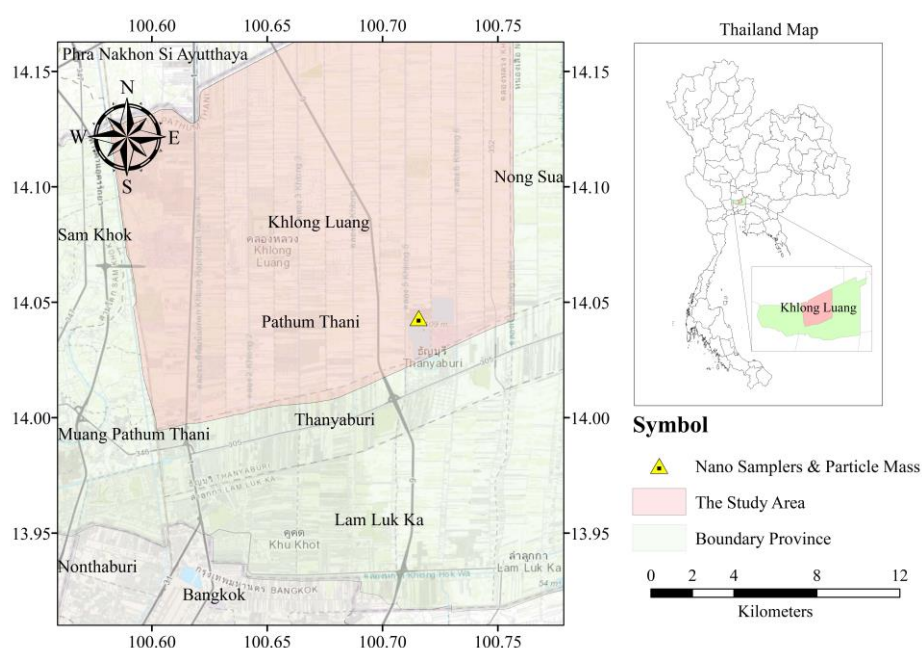


Figure 1. Location of sampling site at the Robotic Innovation and Automatic Mechanical Center, Thailand Institute of Scientific and Technological Research (TISTR), Technotani, Klong Ha, Klongluang, Pathumtani province, Thailand

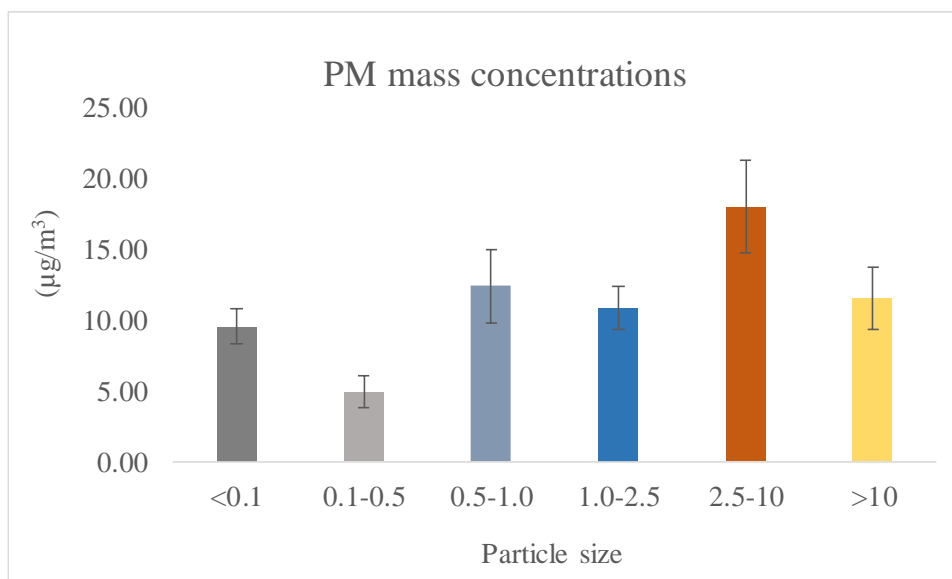


Figure 2. Size-fractionated particles mass concentration in TISTR, Klong Ha, Pathumtani of Thailand.

Table 1 PMs concentration and their ratios during the study period in TISTR, Klong Ha, Pathumtani of Thailand.

Particle size	Mass concentration	Ratio of mass fraction
	(µg/m ³)	(%)
PM _{0.1}	9.57 ± 1.22	14.22
PM _{0.1-0.5}	4.94 ± 1.11	7.34
PM _{0.5-1.0}	12.44 ± 2.58	18.47
PM _{1.0-2.5}	10.86 ± 1.56	16.13
PM _{2.5-10}	18.01 ± 3.27	26.74
PM _{>10}	11.51 ± 2.21	17.10
PM _{2.5}	37.81 ± 3.23	56.16
TSP	67.33 ± 4.24	100

Table 2 Concentrations of OC, EC, Char-EC, Soot-EC, TC (µg/m³), OC/EC and Char-EC/Soot-EC ratio in PM_{0.1} at TISTR, Klong Ha, Thailand.

Particle size	OC	EC	Char-EC	Soot-EC	TC	OC/EC(-)	Char-EC/Soot-EC
PM _{0.1}	0.67 ± 0.15	0.36 ± 0.12	0.12 ± 0.04	0.24 ± 0.08	1.02 ± 0.25	1.95 ± 0.42	0.49 ± 0.05

Table 3 Meteorological parameters

Sampling Date	Temperature (°C)	Relative humidity (%)	Pressure (mmHg)	Rainfall (mm)	Wind speed (knot)	Wind direction (degree)
10/5/2017	27.30	87.00	756.59	-	2.00	70.00
10/7/2017	28.60	85.00	755.74	2.60	3.00	70.00
10/9/2017	29.40	81.00	754.32	-	3.00	320.00
10/16/2017	29.70	73.00	754.60	0.80	4.00	230.00
10/18/2017	28.50	80.00	757.04	-	2.00	10.00
10/20/2017	30.50	76.00	757.75	-	2.00	320.00
Mean	29.00	80.33	755.89	0.57	2.67	-
SD	1.11	5.28	1.49	1.05	0.82	-
Min.	27.30	73.00	754.32	0.00	2.00	-
Max.	30.50	87.00	757.75	2.60	4.00	-

The value in the table are data which provided from Department of Thailand Meteorology.

Table 4 Correlation between meteorological factors and PM_{0.1}.

Particle size	Temperature (°C)	Relative humidity (%)	Pressure (mmHg)	Rainfall (mm)	Wind speed (knot)
PM _{0.1}	0.395	-0.463	-0.004	-.820*	-0.092

The number in the table are regression slope; the statistically significant value at $p < 0.05$ are bloded; * and ** for the confident level of 0.01 and 0.05.

Conclusion

In this study, particle-bound carbon consisting of OC and EC in size-classified particles down to the size of nanoparticles (NPs) was examined at sub-urban area of Bangkok, Thailand, during October (wet season) 2017. The carbon species were evaluated by a thermal/optical reflectance method. The average PM concentration in size-specific PMs was found to be high in the sub-urban area. The average concentration of PM_{0.1} in sub-urban area was found to be 9.57 $\mu\text{g}/\text{m}^3$ in the rainy season, whereas PM_{0.1-0.5} was 14.57 $\mu\text{g}/\text{m}^3$. This finding suggested that the average concentration of PM_{0.1} was greater than 50% of the concentration of PM_{0.1-0.5}. When NPs are exposed for an extended period of time, it is probable that they will have a long-term effect on human health. The PM_{0.5-1.0} fraction had the highest OC and EC values. The carbon composition revealed that the average concentration of OC was 0.67 $\mu\text{g}/\text{m}^3$, while the average concentration of EC was 0.36 $\mu\text{g}/\text{m}^3$, implying that OC was more concentrated than EC. This study site's source of NPs can be attributed to biomass burning. In the study period (wet season), the correlations between OC and EC, as well as char-EC and soot-EC, were substantial.

It implies a common combustion source, such as diesel engines. The weak associations imply that carbonaceous aerosols produced during this period is the result of more complicated sources, notably biomass combustion.

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Characterization and Stability Evaluation of Extracted *Mitragyna speciosa* (Kratom) Nanoemulsion

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Abstract:

In Thailand, *Mitragyna speciosa* (Kratom) leaves have been used for enhancing work productivity and especially pain relief, due to the opioid agonistic activities of mitragynine, an indole alkaloid only found in kratom leaves. However, its applications in medicinal and pharmaceutical industries are limited due to its poor aqueous solubility and low stability under light and heat. Therefore, Nanoencapsulation technology is utilized to solve these problems by using an oil in water (o/w) nanoemulsion system. In this work, extracted kratom nanoemulsions were formulated using a low energy method at 60-70 °C. The optimized nanoemulsions consist in form of percent by weight; 2% oil phase, 10-20% surfactant; tween 80, 1% glycerin, and water phase. Prepared nanoemulsions were characterized in terms of appearance, particle size, zeta potential value, polydispersity index (PI), pH value, and their stability. The results showed a decreasing of particle size and PI when the concentrations of tween 80 increased. The particle sizes were about 15-110 nm. Zeta potential values were lower than -30 mV, indicating good stability. In 90 days, larger size of particle in nanoemulsions were observed in longer time storage, high temperature (50 °C), and basic environment. However, zeta potential values of nanoemulsions were slightly changed under these conditions.

1. Introduction

Kratom (*Mitragyna speciosa*) is a local tree found in Southeast Asia in places such as Malaysia and Thailand. Its leaves are generally smoked, freshly chewed, or brewed as tea¹, and traditionally used as a medicine to enhance work productivity, treat pain relief and diarrhea. There are various pharmacological activities, which have gained attention in recent years. In Thailand, Kratom was removed from the list of prohibited substances under Schedule 5 of the Thai Narcotics Act (No.8) B.E. 2564 in 2021, which could then be legally traded, possessed, and consumed. Its consumptive effects are reported to be dose-dependent, functioning primarily as either a stimulant or sedative. Overdose consumption certainly causes undesirable effects such as sweating, vomiting, loss of appetite, and hepatotoxic, and nephrotoxic effects².

Mitragynine is widely known as an indole alkaloid and a major chemical component in kratom leaves, reaching 66%wt of total alkaloids. It is a psychoactive chemical substance that can bind the opioid receptor in the nervous system³. The stimulant effects are cocaine-like, causing more alertness and the ability to withstand prolonged sun exposure in doses smaller than 5 g. As an analgesic (morphine-like) and feelings of pleasure and euphoria are some of the sedative effects at higher doses between 5 g

and 15 g⁴. Accordingly, Kratom leaves are used as a remedy for alleviating opioid withdrawal symptoms because they are easier than drugs to withdraw from. Moreover, phenolic and flavonoid compounds are found in its leaves as well. They are antioxidants that help neutralize or scavenge free radicals, including reactive oxygen species (ROS) that can be generated during metabolic processes in the body or external environments such as pollution, UV radiation, and certain chemicals. Immoderate ROS induces many diseases and damages the skin. Therefore, consuming antioxidants from natural substances in the pharmaceutical, food, supplements, and cosmetics industries is global-trending. Previously, mitragynine and kratom leaves extract were reported as possible active ingredients for anticancer, anti-inflammatory, antibacterial, antinociceptive, and antioxidant activity⁵⁻¹⁰. These researches indicate the possibility of added commercial value from local plants like the kratom tree. However, the application of extracted kratom is still limited by its poor aqueous solubility and low stability under light and heat.

Nanoemulsion is a type of nanoencapsulation. It consists of two immiscible liquid phases such as oil and water, in which one liquid is dispersed within another by surfactants

forming an isotropic colloidal system. Nanoemulsion can be classified as an oil-in-water (o/w) emulsion, in which the oil phase disperses in the water phase, or when the reverse occurs as a water-in-oil (w/o) emulsion. The size range of 50-200 nm leads to a transparent or translucent appearance and Brownian motion with no gravitational separation through kinetic stability. Additionally, phase separation happens over time due to the thermodynamic instability. In previous works, kratom leaves extracts were encapsulated using lipid nanoparticle systems^{11,12}. However, these works were conducted with overly complex procedures and with the relatively high temperatures being the probable cause of the chemicals' decomposition. To encapsulate the kratom leaves extract effectively, it is clear that a simple low-energy method, like nanoemulsion is preferable. Spontaneous or self-emulsification is a commonly used low-energy method, which is dependent on the chemical energy stored in the components of the system to be emulsified without specific devices. The nanoemulsions were created by stirring continuously after the oil and water phases were mixed. This work aims to formulate a stable o/w nanoemulsion for encapsulating kratom leaves extract with simple and low-energy procedures to improve solubility and stability, control the dosage of bioactive compounds, and prolong shelf life.

2. Methods

2.1 Kratom leaves extraction

The maceration method was used in the extraction process. Dried Kratom leaves were ground in powder and soaked in ethanol for 7 days, then the liquid extract was carried out and filtered by vacuum filtration with a 2.5 µm pore size filter paper. A new batch of ethanol was added for the re-soaking process in triplicate. Then, the crude extract was derived by evaporating the liquid extract using a rotary evaporator.

2.2 Preparation of Nanoemulsion

To prepare a crude solution, a crude extract was pre-mixed with jojoba oil and glycerin in a certain amount and stirred on a hotplate magnetic stirrer at 60-70 °C until a homogeneous solution was obtained. Next, the preparation of nanoemulsion was started by combining the weighed crude solution and surfactants (tween 80 and span 80) in a glass vial as an oil phase. This was followed by stirring the mixture at the same temperature with 700 rpm for 10 minutes. After that deionized (DI) water was

dropwise added up to the total amount of 10 grams nanoemulsion and continuously stirred for 5 minutes.

2.3 Characterization and Evaluation

The characterizations of particle size, polydispersity index (PI), and zeta potential value were obtained from the Dynamic light scattering (DLS) technique. The process involves diluting nanoemulsions with DI water 250 times and then analyzing them using the Nanoparticle analyzer (Horiba SZ-100) with a 90° scattering angle at 25±0.5 °C. The average value is calculated from the measurement 3 times repeatedly.

3. Results

3.1 Optimization of Nanoemulsions

To achieve the desired emulsion characteristics, including droplet size, stability, and appearance. Surfactants are indeed essential ingredients in low-energy methods that play a critical role in reducing the surface tension between immiscible phases, such as oil and water. The choice of surfactant and its concentration is a key factor in spontaneous emulsification, which requires very negative free energy and indicates greater thermodynamic stability. The free energy of emulsion formation is expressed in **Scheme 1**¹³. Accordingly, the increment of dispersion entropy is considered by determining the Hydrophile-Lipophile Balance (HLB) value. The HLB ranges from 8-16 are recommended for oil-in-water (o/w) emulsion. Besides, co-surfactants are used for properly promoting dispersibility and solubility.

Tween 80 (HLB = 15) and span 80 (HLB = 4.3) were initially selected as the surfactant and co-surfactant respectively in formulation 1-4. (**Table 1**.) The different ratios of tween 80 to span 80 were investigated as 80:20, 60:40, 40:60, and 20:80. After 16 days of storage, phase separation was observed in all of the formulations. They were quickly separated and had more turbidity when the ratio of span 80 was increased, demonstrating that the lower HLB value of span 80 and HLB_{mix} value showed less dispersion in the water phase. Therefore, the insufficient dispersion entropy probably affected their instability.

$$\Delta G = \gamma \Delta A - T \Delta S$$

Scheme 1. The free energy equation of emulsion formation. Where γ is the interfacial tension of oil-water interface, ΔA is the change in interfacial area, T is the temperature, and ΔS is the change in dispersion entropy.

In contrast, transparent nanoemulsions were collected when tween 80 was used in formulation 5-10. (**Table 2.**) Its HLB value showed good dispersion in the water phase. After the water phase was added to the oil phase that contains the surfactant, the tween 80 molecules aligned themselves at the oil-water interface with their hydrophilic heads facing outward, raising interfacial turbulence and dispersion entropy. This helped to reduce interfacial tension and nano-droplet size. Subsequently, to minimize the concentration of tween 80 its concentration was decreased from 20% to 10%wt, which could lead to a less transparent appearance and shorter storage stability. In 30 days, the results showed that the lower concentrations of tween 80 affected rapid phase separation. The concentrations in the range of 16-20%wt of tween 80 were effective in preventing phase separation and producing non-separated nanoemulsions due to their being above the critical micelle concentration (CMC). There were similar results in formulation 11-16. Their particle size, polydispersity index (PI), and zeta potential values are shown in **Figure 1**. We observed that particle sizes and zeta potential values were reduced when the concentration of tween 80 was increased. Zeta potential values of all formulations indicated great stability at over -30 mV. The increased concentration range of 16-20%wt did not significantly impact the particle size and zeta potential values. Polydisperse size distribution was obtained from polydispersity index (PI) values, which were higher than 0.05.

In comparison, reducing the concentration of glycerin from 2 to 1%wt in formulation 11-16 made nanoemulsions clearer. Glycerin was used as a co-solvent to diminish the viscosity of the oil phase. Its amphiphilic structure also improved the homogeneity. However, excessive amounts of glycerin feasibly interfered with micelle formation and dispersibility of oil droplets. Consequently, using 16-20%wt of tween 80 and 1%wt of glycerin was suitable for preparing extracted *Mitragyna speciosa* nanoemulsion with high stability.

Formulation ^[a]	Tween 80: Span 80 ^[b] (%wt)	Appearance	HLB _{mix}
1	16:4	Separation	12.86
2	12:8	Separation	10.72
3	8:12	Separation	8.58
4	4:16	Separation	6.44

[a] Crude solution contained 1% wt crude extract, 1% wt jojoba oil, 2% wt glycerin with 20% wt total surfactant. [b] Surfactant and co-surfactant

Table 1. Effect of tween 80 to span 80 ratios

Formulation ^[a]	Glycerin (%wt)	Tween 80 (%wt)	Appearance
5	2	20	Non-separation
6	2	18	Non-separation
7	2	16	Non-separation
8	2	14	Separation
9	2	12	Separation
10	2	10	Separation
11	1	20	Non-separation
12	1	18	Non-separation
13	1	16	Non-separation
14	1	14	Separation
15	1	12	Separation
16	1	10	Separation

[a] Crude solution contained 1% wt crude extract, 1% wt jojoba oil, 1% wt glycerin

Table 2. Effect of tween 80 and glycerin concentrations

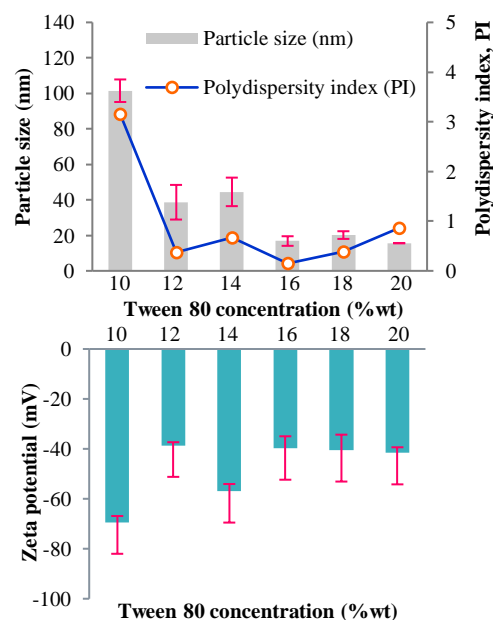


Figure 1. Effect of tween 80 concentration on particle size, polydispersity index, and zeta potential value in formulations 11-16 after preparation for 1 day.

3.2 Stability Evaluation

Nanoemulsions are kinetically stable. Their small particle size can cause disability such as flocculation, coalescence, Ostwald ripening, and creaming. In this experiment, an optimized nanoemulsion was chosen and repeated to evaluate the stability by maintaining a uniform dispersion under different conditions. There were the effects of storage time, temperature, and pH of the environments. The physical changes were detected by the DLS technique.

3.2.1 Effect of Storage Time

The storage time is a critical factor in stability. In particular, nanoemulsions are prepared by the low-energy method, which is merely stabilized by utilizing the internal chemical energy of surfactants. To explore the effect of storage time, the nanoemulsion was stored at room temperature (30 °C) for 1, 21, and 90 days. The results showed great stability over an extended period of 90 days without phase separation. However, less transparent nanoemulsion was observed with longer time storage. (**Figure 2.**) In 21 days, the particle size was slightly changed compared with the initial nanoemulsion of 15.6 ± 0.10 nm. However, after 90 days of storage, particle size increased significantly. Perhaps Oswald ripening and coalescence were causes of larger particle size and turbidity leading to a wide range of size distribution. However, the negligible change of zeta potential values indicated high stability.

3.2.2 Effect of Temperature

Nanoemulsions are thermodynamically unstable. The temperature was a kind of external heat energy affecting the stability of the nanoemulsion. In this phase, the nanoemulsion was divided into 3 parts and stored at different temperatures (4, 30, and 50 °C) for 7 days. (**Figure 3.**) The higher temperature rapidly increased particle size and decreased zeta potential value in a short period. Furthermore, it led to a more rapid and energetic movement of oil droplets, and particle aggregation probably happened through collision. Hence, the lower temperature produced a better storage condition for prolonging the nanoemulsion's stability.

3.2.3 Effect of pH value environment

The chemical properties of nanoemulsions, particularly their surface charge and tolerance to electrical charge interruption, are factors that influence their stability. At the beginning, the pH value of the nanoemulsion was measured as 3.85, which placed it in an acidic range. After that, it was divided for examination into various pH value environments (pH 3, 7, and 9). (**Figure 4.**) In pH 3, the particle size was slightly altered when compared with the controlled nanoemulsion and more stabilized than in pH 7, and 9 respectively. This observation suggested nanoemulsion did not tolerate chemical charges environments like protons (H^+) and hydroxide ions (OH^-) because the chemical charges on the particle's surface was disturbed. The electrostatic repulsion of protons possibly occurred which reduced the particle size in the acidic

environment, whereas in more basic environments at pH 7 and 9, the opposite electrical charges of the protons and hydroxide ions may have caused the electrostatic attraction generating the larger particle size. In pH 9, the electrostatic repulsion of excessive hydroxide ions feasibly reduced particle sizes. The addition of chemical charges also influenced variance size distribution. Nonetheless, the nanoemulsion kept its good stability, which was observed in the slight change of zeta potential value.

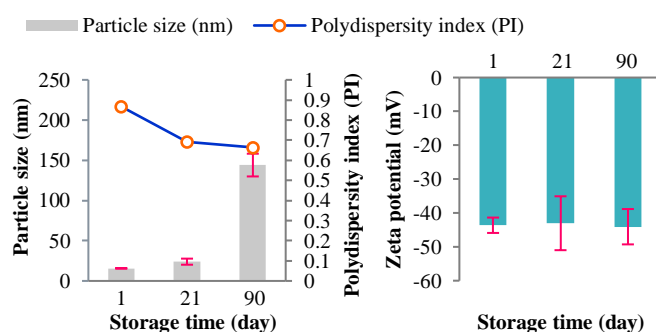


Figure 2. Effect of storage time on particle size, polydispersity index, and zeta potential value.

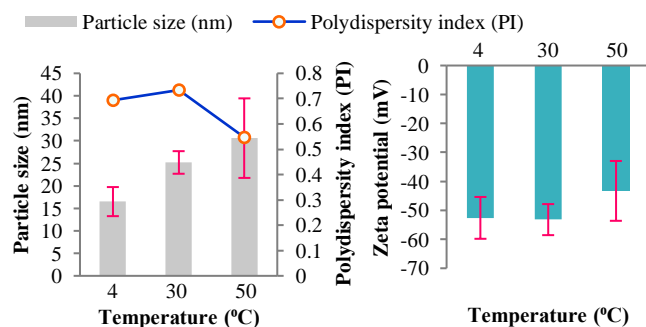


Figure 3. Effect of temperature on particle size, polydispersity index, and zeta potential value.

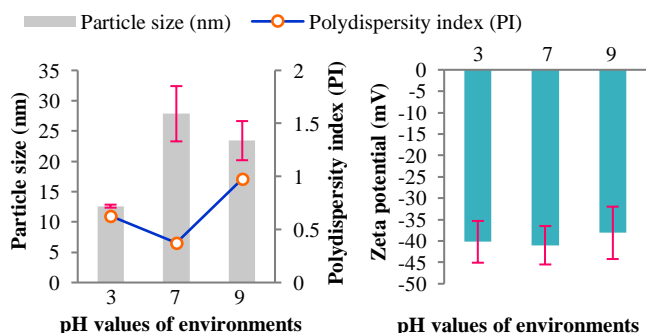


Figure 4. Effect of pH values of environments on particle size, polydispersity index, and zeta potential value.

Conclusion

In conclusion, extracted *Mitragyna speciosa* (Kratom) nanoemulsion can be formulated using spontaneous emulsification with 16-20% wt of tween 80, forming dark green transparent o/w nanoemulsions to enhance the solubility of the bioactive compounds in kratom leaves. Furthermore, the stability evaluation of prepared nanoemulsions under extended storage time, high temperature, and different pH value environments confirm their great stability and shelf life's prolongation for utilization in many industries.

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