Research Article

Electrochemical Behavior and Electronucleation of Copper Nanoparticles from CuCl$_2$·2H$_2$O Using a Choline Chloride-Urea Eutectic Mixture

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Received 4 May 2021; Revised 18 June 2021; Accepted 3 July 2021; Published 19 July 2021

Academic Editor: Thanh Dong Pham

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This work presents a thorough study on the early stage of copper electrodeposition from a choline chloride-urea deep eutectic solvent (DES). Determination of possible species in DES containing Cu$^{2+}$ ions as the electrolytes has been performed using UV-Vis measurements. Kinetic and thermodynamic aspects of copper electrodeposition on glassy carbon electrode from DES were thoroughly investigated using cyclic voltammetry (CV) and chronocoulometry (CA). Both results from CA and CV have demonstrated that the copper electrodeposition could be performed directly from DES containing a small amount of water by the single potentiostatic step technique. Theoretical approach confirmed that the direct electronucleation of copper nanoparticles in the DES can be described by a model with two contributions, namely, (i) adsorption process and (ii) a three-dimensional (3D) nucleation and diffusion-controlled growth of copper nuclei, to the total current density transients. Kinetic parameters are important for controlling morphology and chemical composition of the obtained nanoparticles, which are verified by surface characterization techniques such as SEM and EDS.

1. Introduction

Copper nanoparticles (Cu-NPs) are of great interest for applications in many engineering fields, including electronics, energy, catalyst, environment, and agriculture, owing to their natural abundance, low cost, and diversity of preparation methods [1, 2]. Some (typical) examples can be mentioned such as the use of Cu-NPs in sensors [3], fuel cell, and solar cell [4, 5] and in conductive inks for printed electronics [6]. In agriculture, Cu-NPs have also shown important effect in regulating plant growth and development and increasing chlorophyll formation and seed production [7]. Moreover, due to their fungicidal and insecticidal activity against the pests of crop plants, they can be used as nano-pesticides, nano-herbicides, nano-fertilizers [8, 9], among others. These benign behaviors of Cu-NPs make the study on their synthesis a topic of current interest.

It is known that Cu-NPs can be produced by different routes, physical methods, or chemical methods [10]. The main concern is the fact that these methods are neither cost-effective nor eco-friendly due to the use of toxic
The electrochemical synthesis of Cu-NPs from a “green” solvent such as a deep eutectic solvent (DES) based on choline chloride could be a promising candidate to tackle these problems.

DESs have received much attention for metals electrodeposition applications (i.e., Ni, Fe, Al, and Zn [12–16]) due to several advantages, such as a wide electrochemical window, low cost, ease of preparation, negligible vapor pressure, thermal stability, and (nearly) null hydrogen liberation during electrodeposition [17, 18], compared to conventional aqueous solvents. Particularly, in the case of copper, although the copper electrodeposition from DESs has been reported in the literatures [19, 20], insights on the early stages of this process, specifically, mechanistic and kinetic aspects, are still limited. Abbott et al. [19] have first studied the copper electrodeposition in the eutectic mixture of choline chloride and ethylene glycol (ethaline) and found that copper reduction occurs via two well separated one-electron stages: Cu(II)–Cu(I)–Cu. These processes have been studied by Sebastián et al. [20] using Cu(I) and Cu(II) solutions dissolved in aqueous solvent and in the mixture of choline chloride and urea (reline), DES. They proposed the use of the double potentiostatic step technique to separate current densities related to the reduction of each copper species. However, there have been some concerns in the application of this technique and unsolved problems as follows: (i) it can be facilitated in a medium with the low mobility of species (such as the reline DES under their studied conditions), but it is difficult in medium with the good mobility of ionic species (i.e., aqueous medium); (ii) success of the procedure is dependent on control of the initial conditions at which electrodeposition takes place [20], (iii) effect of residual water in DES has not been considered, while several recent papers [21, 22] have reported that a small amount of water can influence physiochemical properties, the dynamics, and the electrochemistry of active species (i.e., decreasing the viscosity and resistivity of the DES and altering the speciation of the copper chloro-complexes) [22, 23]; and (iv) although Sebastián et al. [20] have reported some initial results on the copper electroneucleation in DES using cyclic voltammetry (CV) and chronoamperometry (CA), insights on the mechanisms and kinetics including mathematical models capable of describing the Cu nucleation and growth processes from DES in practical conditions where it can contain some unavoidable small amounts of residual water adsorbed from the environment or DES preparation, and some important kinetic parameters such as the nucleation frequency, \( A \), the number density of active sites for copper nucleation onto the electrode surface, \( N_0 \), have been not determined. Consequently, the knowledge on these aspects must be updated; in addition, (v) details on the speciation of copper ions dissolved in DES and the possibility of using the conventional potentiostatic method to electrodeposit copper from DES have not yet been studied.

Therefore, the aim of this work is to study the nucleation and growth mechanisms and kinetics of copper deposition process on glassy carbon electrode from the reline containing Cu\(^{2+}\) ions as the electrolyte solution using both theoretical and experimental approaches. UV-Vis spectra were used to analyze the species containing in Cu\(^{2+}\) electrolyte solution.

2. Materials and Methods

2.1. DES and Electrolyte Preparation. Chemicals such as choline chloride (\( \text{C}_5\text{H}_{11}\text{ClNO} \), 97%, Sigma-Aldrich), urea (\( \text{CH}_3\text{N}_2\text{O} \), 99%, Sigma-Aldrich), and copper (II) chloride hexahydrate (CuCl\(_2\cdot\text{H}_2\text{O} \), ACS reagent, \( \geq 99.0\% \)) were used. DES was prepared by mixing choline chloride and urea in a 1:2 molar ratio at 100°C. This obtained mixture was constantly stirred until a transparent and homogenous solution was obtained. Details of DES preparation can be found in our previous study [24]. The Cu\(^{2+}\) electrolyte solution was obtained by adding 50 mM copper (II) chloride hexahydrate salt, to the DES, and the solution was stirred for 12 hours at 60°C. The obtained electrolyte solution was kept in a dehumidifier for latter electrochemical measurements. The water content of CuCl\(_2\cdot\text{H}_2\text{O} \) dissolved in DES was measured by Karl Fischer coulometric titration, using a Titrino Coulometer (Model 756, Metrohm), giving a value of about 0.35%.

2.2. UV-Vis Measurements. UV-Vis measurements of the electrolytes containing Cu(II) dissolved in DES were performed in an UV-Vis spectrophotometer (UV-6850, JENWAY Double Beam Spectrophotometer). UV-Vis spectra of the solution were obtained for different temperature (25°C to 50°C) in a quartz cell with a light path length of 1.0 cm using the Prism 5.51 PC software coupled to the equipment.

2.3. Electrochemical Tests. A conventional water-jacketed cell comprising three electrodes was used for CV and CA tests. The electrochemical cell was composed of a glassy carbon electrode (GCE), with 0.0707 cm\(^2\) surface area as the working electrode, a platinum wire, and a silver wire as counter and
Figure 2: Continued.
The electrochemical cell temperature was controlled by a Lauda RMS 179 Circulator with RM6 Refrigerating Water Bath Chiller, −15 to 100°C (with a temperature stability of ±0.02°C). CA and CV measurements were carried out using VersaStat 3 system, coupled to the VersaStudio software installed in a PC for experimental control and data collection. These experiments were performed at 70°C.

2.4. Surface Analysis Characterization. Morphological and chemical compositions of the electrodeposits were characterized using field emission scanning electron microscope (FE-SEM), Model JEOL JSM SEM 7000F, and energy-dispersive X-ray spectroscopy (EDS), respectively, to confirm the existence of Cu-NPs on the GCE surface.

3. Results and Discussion

3.1. Copper Speciation in the Reline. A drastic change in color of Cu²⁺ ions dissolved in DES from blue to green before and after heating (see Figure 1) can be observed with the naked eyes. The green color of the Cu²⁺ electrolyte solution remains unchanged and becomes stable after heating. This phenomenon is able to be recorded by UV-Vis spectra as shown in Figure 1. It reveals two peaks in the UV region, at 246 nm and 298 nm, which can be assigned to the presence of species such as [CuCl₄]²⁻ [25]. Meanwhile, in the near infrared (NIR) region, a broader peak between from 705 to 755 nm and a sharp peak at 1022 nm are detected, which can be due to the presence of [Cu(H₂O)₆]²⁺ species [26]. By increasing the temperature, the absorbance peaks tend to shift to higher value of wavelength (inset of Figure 1). These results confirm the presence of different complexes in DES such as [Cu(H₂O)₆]²⁺ and [CuCl₄]²⁻ species corresponding to room temperature and higher temperature, respectively. Thus, at room temperature, [Cu(H₂O)₆]²⁺ can be predominant due to the small amount of residual water in DES, which is due to the use of CuCl₂·2H₂O salt and/or atmospheric moisture. After heating, this water tends to evaporate, and Cl⁻ ions can substitute (partially) the H₂O ligands to form [CuCl₄]²⁻ complexes. The color change of CuCl₂ solution in choline chloride-based DESs has been also observed in other studies [22, 26], where CuCl₂(hyd.) dissolved in ethaline exhibits yellow color, typical of forming [CuCl₄]²⁻ species, and by adding water to the solution it shifts from yellow to blue. According to Valverde et al. [22] and Vreese et al. [26], this color change can be explained due to the substitution of Cl⁻ by H₂O ligand. Therefore, the general species of CuCl₂·2H₂O dissolved in reline could be presented in form of the mixed chloro-aqua chemical complex structure [CuClₓ(H₂O)ₙ]^{(2-x)⁻}, where n + m = 4 → 6 and x = 0 → 6 [22, 26].

3.2. CV Study. Figure 2(a) shows the CVs recorded on the GCE in DES (discontinuous curve) and GCE/50 mM Cu(II) in DES at 70°C. The scan was started at a potential of 0.40 V in the negative direction with a scan rate of 10 mVs⁻¹. CVs recorded onto GCE using different scan rates and cathodic peak current density (jₚ) as a function of the scan rate (v¹/²) at 70°C for (b) peak I, (c) peak II, and (d) peak III.
Figure 3: Continued.
According to Sebastian et al. [20], the first two peaks can be assigned to the transition process from Cu\(^{2+}\) to metallic Cu associated with the reactions, (1) and (2):

\[ \text{Cu}^{2+}_{\text{DES}} + e^- \rightarrow \text{Cu}^+_{\text{DES}} \quad (1) \]

\[ \text{Cu}^+_{\text{DES}} + e^- \rightarrow \text{Cu}_{(s)} \quad (2) \]

The water reduction reaction to hydrogen associated with peak III observed in the CV (Figure 2(a)) can be given by (3) [23]:

\[ 2\text{H}_2\text{O}_{\text{DES}} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (3) \]

Meanwhile, in the backward scan, the oxidation peak located in the potential range of -0.40 V to 0.05 V can be attributed to the oxidation reaction of Cu metallic nuclei
(see (4)) previously formed by (2) during the forward scan. The other peak located at 0.28 V–0.80 V (peak V) can be associated with the oxidation reactions of Cu$^{+\text{DES}}$ from (1), as given in (5).

\[
\text{Cu}_0 \rightarrow \text{Cu}^{\text{DES}} + e^- \quad (4)
\]

\[
\text{Cu}^{+\text{DES}} \rightarrow \text{Cu}^{2+\text{DES}} + e^- \quad (5)
\]

At potentials larger than the potential ranges of peaks III and V, at the extremes of the CV, the current intensity growths are known as the decomposition reactions (reduction and oxidation, respectively) of the solvent [17, 27]. Since this work deals with the copper electronucleation, the reduction reactions, such as (1) and (2), are paid more attention.

To investigate the electrochemical behavior of the system GCE/50 mM Cu(II) in DES, CVs are carried out at different scan rates ranging from 10 to 100 mVs$^{-1}$. It reveals that cathodic peak current density ($j_{cp}$) increments with as the scan rate increases. By plotting $j_{cp}$ as a function of square root of the scan rate ($v^{1/2}$) for three peaks I, II, and III (see Figures 2(b)–2(d)), it can be clearly seen that $j_{cp}$ of these peaks exhibits a linear relationship with $v^{1/2}$. This means that the Cu electrodeposition on GCE from DES follows a diffusion-controlled mechanism, which can be described by the Berzins-Delahay equation [28]:

\[
j_{cp} = \frac{0.61 \times (Fn)^{3/2} C_0 (Dv)^{1/2}}{(RT)^{1/2}}, \quad (6)
\]

where $F$ is the Faraday constant, $R$ is the ideal gases constant, $n$ is the total number of electrons transfer, $C_0$ (mol cm$^{-3}$) is the bulk concentration of reduced species, $D$ (cm$^2$s$^{-1}$) is the diffusion coefficient of Cu(II) ions, and $T$ (K) is the temperature of medium.

According to the CV, copper electrodeposition mechanism must be occurred in two steps through (1) and (2). Therefore, from peaks I and II of interest, there are two values of diffusion coefficient to be determined, $D_I$ and $D_{II}$, correspondingly. $D_{II}$ can be calculated from Eq. (6) and using the slopes of Figure 2(b) and the initial concentration $C_0 = 0.05$ M; thus, $D_1 = 9.9536 \times 10^{-8}$ cm$^2$s$^{-1}$. $D_{II}$ is more difficult to determine since Cu$^+$ concentration is unknown. Fortunately, in the same DES, concentration, and working temperature, Sebastian et al. [29] have proposed a methodology to estimate the surface concentration ($C_s$) of Cu$^+$ ions using the double step technique, which yields $C_s = 0.01694$ M. Taking into account the $C_s$ and the slope values of Figure 2(c), from Eq. (6), it can be derived $D_{II} = 8.67 \times 10^{-7}$ cm$^2$s$^{-1}$ for peak II. These values are consistent with those reported by Sebastian et al. [29] and Popescu et al. [30].

3.3. Potentiostatic Study. Figure 3 depicts CA curves recorded on the GCE at 70°C using the potential range defined from CV (Figure 2(a)). In general, a clear distinction of nucleation mechanisms can be observed from CAs of the studied reduction peaks. Figures 3(a) and 3(b) depict the CAs with a typical Cotrellian behavior, while the CA shapes of Figure 3(c) suggest that the early stage of the Cu electrodeposition onto GCE from DES could follow the three-dimensional (3D) nucleation and diffusion-controlled growth [32]. This demonstrates that direct electrodeposition of copper from DES is evident by simply using the single potential step. The direct electrodeposition of copper in this work refers to the single potential step or the conventional chronoaamperometry, by applying only one potential pulse to deposit copper from Cu$^{2+}$ to Cu, as be illustrated by the following mechanism, (7):

\[
\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ + e^- \rightarrow \text{Cu} \quad (7)
\]

In difference with Sebastian et al. [20], who have stated that (7) could be difficult, Figure 3(d) clearly indicates that both (single and double pulse) techniques can be performed successfully to electrodeposit copper from DES in our case. Interestingly, while the double potentiostatic steps can separate the reduction reactions of each copper species, the single pulse seems to be more advantageous by shortening the reaction time of (1), transition from Cu$^{2+}$ to Cu$^+$, which results in a more complex shape of the experimental CA with an additional (adsorption) contribution to the total current transient density. This process can be explained due to the presence of the residual water containing in the DES, which significantly influences.
Figure 5: Comparison between the CAs (circle) (lines) recorded in the system GC/50 mM CuCl$_2$ in DES at the potentials (from -0.57 to -0.62 V with a step = -0.01 V), and the theoretical transients (line) obtained after fitting Eq. (12) to the experimental data. The inset of Figure 5 illustrates the Cottrell analysis ($j - t^{-1/2}$ plot) of the CA at -0.57 V.

Table 1: Best-fit parameters obtained from fitting Eq. (12) to the experimental data.

| $E$ (V) | $10^3 P_1$ (A cm$^{-2}$) | $P_2$ (s$^{-1}$) | $A$ (s$^{-1}$) | $10^3 P_4$ (A cm$^2$) | $P_5$ (s$^{-1}$) | $10^6 N_0$ (cm$^2$) | $10^7 D$ (cm$^2$ s$^{-1}$) | $10^7 AN_0$ (s$^{-2}$ cm$^{-2}$) |
|--------|-------------------------|-----------------|--------------|----------------------|-----------------|---------------------|------------------------|-------------------------------|
| 0.57   | 3.394 ± 0.002           | 1.065 ± 0.093   | 4.031 ± 0.072| 2.492 ± 0.028        | 1.267 ± 0.158   | 9.232 ± 0.806       | 3.889 ± 0.005          | 3.722 ± 0.075                |
| 0.58   | 3.424 ± 0.002           | 1.143 ± 0.071   | 3.894 ± 0.079| 2.647 ± 0.021        | 1.391 ± 0.132   | 9.741 ± 0.605       | 3.956 ± 0.005          | 3.793 ± 0.081                |
| 0.59   | 3.463 ± 0.002           | 1.346 ± 0.081   | 4.902 ± 0.123| 3.117 ± 0.020        | 1.668 ± 0.148   | 11.217 ± 0.667      | 4.047 ± 0.005          | 5.499 ± 0.141                |
| 0.60   | 3.482 ± 0.002           | 1.533 ± 0.102   | 5.594 ± 0.128| 3.428 ± 0.024        | 1.880 ± 0.174   | 12.632 ± 0.840      | 4.091 ± 0.005          | 7.066 ± 0.166                |
| 0.61   | 3.428 ± 0.002           | 1.746 ± 0.146   | 6.899 ± 0.126| 3.486 ± 0.030        | 2.102 ± 0.235   | 14.846 ± 1.241      | 3.966 ± 0.005          | 10.242 ± 0.196               |
| 0.62   | 3.463 ± 0.002           | 2.519 ± 0.058   | 6.578 ± 0.461| 3.982 ± 0.025        | 3.540 ± 0.261   | 20.976 ± 0.483      | 4.049 ± 0.005          | 13.799 ± 0.967               |

Table 2: Diffusion coefficient calculated using the Cottrellian behavior (see the parameter $P_1$ in Eq. (9)) for different reduction peaks.

| Cottrell analysis | Peak I | Peak II |
|-------------------|--------|---------|
| $10^{-7} D$ (cm$^2$ s$^{-1}$) | 2.0452 | 7.9493  |

The parametric form of the SM model associated with the 3D nucleation and growth is given by [31]:

$$j(t)_{3D} = P_1 t^{-1/2} \left(1 - \exp \left( -P_2 t \right) \right),$$

(9)
Figure 6: Separation of individual contributions to the total current density transient using Eq. (12) for different applied potentials: (a) -0.57 V; (b) -0.58 V.
where

\[ P_1 = \frac{zFD^{1/2}C_0}{\pi^{1/2}}, \]
\[ P_2 = N_0\pi D \left( \frac{8\pi MC_0}{\rho} \right)^{1/2}, \]
\[ P_3 = A, \]

where \( \rho \) is the density of the Cu deposit and \( M \) is its atomic mass, \( N_0 \) is the number density of active sites on the electrode surface, and \( A \) (s\(^{-1}\)) is the nucleation frequency per active site.

The adsorption contribution can be expressed by [31]:

\[ j(t)_{\text{ads}} = P_4 \exp(-P_5 t), \]
\[ P_4 = \frac{E}{R_s}, \]
\[ P_5 = \frac{1}{R_sC}, \]

where \( E \) is the applied potential (V), \( R_s \) is the solution’s resistance (\( \Omega \)), and \( C \) is double layer capacitance (F). Therefore, total contribution to the current density transients shown in Figure 4 is given by:
Thus, the validity of the proposed model. Besides, the average value increases with the increase of the potential, confirming the validation of the derived kinetic parameters, as shown in Table 1, such as $A$ and $N_0$ consistent with the trend of metallic nucleation as observed in the literature [24, 30, 34]. Thus, $N_0$ product increases with the potential, confirming the validity of the proposed model. Besides, the average value of the diffusion coefficient, $D$, is in order $4 \times 10^{-7}$ cm$^2$ s$^{-1}$, which is lower than the result obtained from the CV. However, this is acceptable because it is consistent with several works [24, 29] reported on electrodeposition of other metals in the same DES. Therefore, the use of other methods is necessary as can be seen latter in Cottrell analysis.

To verify the results obtained by CV and Eq. (9), a Cottrell analysis was done to derive the diffusion coefficient from CAs by linearization of longer time after the peak (the falling part) of the transients depicted in Figure 5. Thus, according to the procedure given in to Palomar-Pardave et al. [34] when $t > t_m$ the transient follows the Cottrell equation (see the red line in the inset of Figure 5), in contrast ($t < t_m$) the CA deviates from that behavior. The diffusion coefficients calculated for the transients of the three peaks are shown in Table 2. It reveals that in general the average values of $D$ are higher than the previous results from the CV and fitting Eq. (9) to experimental data. But they are still in the order and agree with the CV method in the increasing trend of $D$ as the potential becomes more negative.

Applying Eq. (12), it is possible to separate the individual contribution of adsorption and 3D nucleation + diffusion-controlled growth of copper in DES to the total current density transients, as shown in Figure 6. It clearly shows that the current densities corresponding to the adsorption effect (Figure 7(a)) tend to reduce as the potential becomes more negative (increasing in magnitude), while the (peaks) current densities related to $j(t)_{3D}$ (Figure 7(b)) increase with the applied potentials. These results validate that the use of the proposed model is suitable for the case of copper electrodeposition on the GCE from reline DES.

3.4. SEM and EDS. Figure 8 shows SEM images of GCE surfaces obtained after electrodeposition with the applied potentials corresponding to region associated with different reduction peaks I, II, and III. It reveals clearly that peak I exhibits a surface with the absence of metallic copper, black color, the same color as seen in a bare GCE surface (see Figure 9(a)), while both peaks II and III result in formation of (copper) NPs, which are verified by EDS spectra depicted in the right-hand side of Figures 9(a)–9(c). But it seems to be not efficient using the potentials at peak III due to the hydrogen evolution reaction (see (3)). Moreover, these verify the reduction reactions proposed in the CV analysis. Thus, according to the speciation results and the mechanisms derived from CV and modeling analysis, the nanoparticles observed in Figure 9(c) should be associated with the mixture of Cu/Cu(OH)$_2$ as the core/shell structure due to the presence of OH- ions in (3), as similar to the mechanism of Ni electrodeposition from reline reported in other studies [35, 36]. As suggested from the SEM image depicted in Figure 9(b) showing the formation of metallic (copper) nuclei with different sizes and ages, the copper electrodeposition process onto the GCE from DES containing a small amount of water follows to the progressive nucleation mechanism. This could be explained due to the contribution of the adsorption process, which occur first in the short time of the CA, giving rise to the formation of the first nuclei on the electrode surfaces.

It is worth mentioning that the Cu-NPs obtained using the potential around peak II are denser than those obtained from peak III giving more porous and larger particle size.
This is extremely useful for further applications (i.e., biosensors, microelectromechanical systems, and MEMS) of the copper electrodeposition from DES since one can select the (appropriate) conditions to obtain desired surface morphology, structure, and chemical composition.

4. Conclusions

The electrochemical synthesis of Cu-NPs from DES reline (containing a small amount of water, ~0.35%) was thoroughly studied. From the UV-Vis spectra measurements, a sudden change in color of Cu$^{2+}$ electrolytes solution from blue to green was observed by heating the solution from room temperature to above 40°C. This can be associated with the presence of complex species such as $[\text{CuCl}_n(\text{H}_2\text{O})_m]^{(2-x)^-}$, where $n + m = 4 - 6$ and $x = 0 - 6$. A wider potential range (compared to the literature) observed from the recorded CV on the system GCE/50 mM Cu(II) in DES, which exhibits more complex behavior with three reduction peaks (see (1), (2), and (3)). By means of the CA technique, it was possible to distinguish the electrochemical behavior of these processes, indicating that peak I corresponds to the reduction of intermediate (soluble) species (Cu(II) to (Cu(I)), (1)); peak II corresponds to the formation of metallic copper from soluble species ((Cu(I)) to Cu(0), (2)), and peak III could be occurring simultaneously both reactions, namely, hydrogen
evolution reaction of small amount of water containing in DES and (2). From these results, it has verified that the copper electrodeposition can be performed by the single potentiostatic step route. A model, comprising two contributions, 3D nucleation and diffusion-controlled growth + adsorption, was proposed and validated to explain the copper electrodeposition on the GCE from the reline DES. These kinetic and mechanistic aspects play the key role in controlling morphology, structure, and chemical composition of Cu-NPs, which are verified by surface characterization techniques using SEM and EDS. Finally, SEM images have verified that the copper electrodeposition from DES containing a small amount of water follows the progressive nucleation mechanism.

**Data Availability**

The data used to support the findings of this study have not been made available because it is part of an undergoing project.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

**Acknowledgments**

This research is funded by the Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.02-2019.28.

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