http://dx.doi.org/10.5935/0103-5053.20150074

J. Braz. Chem. Soc., Vol. 26, No. 6, 1115-1123, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Effect of Applied Voltage on Slow-Release of Cu(II) Ions on the Synthesis of Copper(II) Stearate Complex by Electrochemical Technique

Norazzizi Nordin,[a] Siti Z. Hasan,[a] Zuhailie Zakaria,[a] Noor A. Baharuddin,[a] Wan Z. Samad,[a] Muhammad R. Yusop[a,b] and Mohamed R. Othman,[a]*

[a]*School of Chemical Sciences & Food Technology, Faculty of Science & Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia*

[b]*Regenerative Medicine Cluster, Advanced Medical & Dental Institute, Universiti Sains Malaysia, 13200 Kepala Batas, Pulau Pinang, Malaysia*

An electrochemical technique based on the slow-release of Cu^{2+} ion from electrochemical oxidation of a Cu anode in the presence of stearic acid (HSt) and an aqueous solution of ammonium acetate (CH_3COONH_4) (0.1 mol L^{-1}) as supporting electrolyte has been used to synthesize Cu(II) stearate (Cu(II)St) complex. Different values of applied voltages (1, 5 and 10 V) were used during the synthesis to study the effect of applied voltage on the particle size of the Cu nanoparticles and morphology of the synthesized Cu(II)St complex. By using 1 V of applied voltage, small Cu nanoparticle was produced with an average particle size of 2.49 ± 0.82 nm, followed by 5 V (3.61 ± 1.18 nm) and 10 V (6.64 ± 2.72 nm). Another advantage of using 1 V of the applied voltage is the formation of well-shaped petal-like structures of the Cu(II)St complex compared to the synthesis using 5 V and 10 V which inhibit the formation of well-shaped petal-like structure. This proves that the slow-release electrochemical synthesis using lower value of applied voltage has successfully resulted in the formation of small size Cu nanoparticles.

Keywords: electrochemical synthesis, Cu(II) complexes, applied voltage, nanoparticle

Introduction

Copper(II) carboxylates have received considerable attention during the last decades due to their special features in geometrical structures and physicochemical properties, and they have many applications in biochemistry and in industry. Cu(II) carboxylates have been applied as superhydrophobic coating materials,[1,2] precursors in the synthesis of metal-organic frameworks,[3] and as molecular templates in the synthesis of semiconductor nanorods.[4] In addition, Cu(II) carboxylates with nitrogen donor ligands have been reported to play an important role in fungal growth retardation activity for wood protection.[5]

The interest of these complexes derives from the diversity of its structure, as it can contain two or more antiferromagnetically coupled metal centers.[6,7] Each carboxylate oxygen atom in the complex has two lone electron pairs. The structural formation of the complex depends on the utilization of one or two lone electron pairs on the oxygen of the carboxylate group for bonding to the Cu^{2+} ion. If only one lone electron pair is involved, the result is a paddle-wheel dimer structure (Figure 1a). A polymeric structure (Figure 1b) may form if the second lone pair is donated to the Cu^{2+} ion of another paddle-wheel dimer structure.

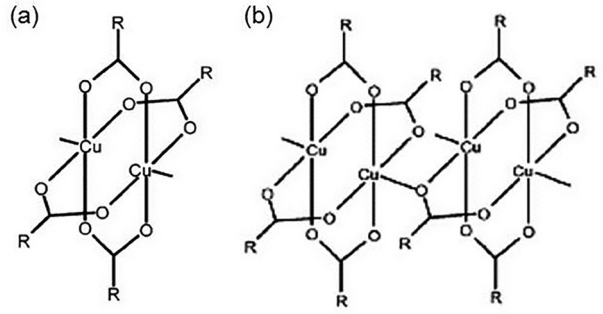


Figure 1. Structure of (a) paddle-wheel dimer and (b) a polymeric dimer of Cu(II) carboxylates.

In such a dinuclear dimer, two Cu^{2+} ions are bridged by four carboxylate groups of ligands. The coordination geometry around Cu atoms in the paddle-wheel dimer Cu(II) carboxylate is square pyramidal with D_{4h}

*e-mail: rozali@ukm.edu.my

symmetry.[8] There are two axial positions in the paddle-wheel dimer that can be occupied by a wide variety of ligand donors or electron pairs. The common axial ligands most reported in the literature are water,[9] urea,[10] pyridine-carboxylates,[11] and organic acid.[12] In many cases, axial ligation of the paddle-wheel dimer prevents formation of inter-dimer bridges, due to donation of the lone electron pair of carboxylate oxygen to the Cu^{2+} ions of the neighboring paddle-wheel dimer. Consequently, formation and precipitation of a paddle-wheel dimer with polymeric behavior can be avoided.[13]

Previous studies have reported that most of the complexes are synthesized using chemical methods. Often, Cu(II) sulfate is used to synthesize the complexes with corresponding carboxylic acid,[1,7,10] though other compounds of Cu(II) such as carbonate,[14,15] oxide[6] and nitrate[8] have been used. Other than Cu(II) salts, copper plates also have been used as a Cu^{2+} ion source.[2] In the current paper, Cu(II)St complex was prepared using an electrochemical technique based on the reaction between Cu^{2+} ions from the electrochemical oxidation of Cu anode with palm-based stearic acid (C18:0) to produce Cu(II)St complex.

This electrochemical technique offers several advantages in inorganic synthesis: (*i*) the ability to achieve oxidizing or reducing power that cannot be equaled by any ordinary chemical reagent; (*ii*) no contamination to a solution with a reducing agent (or oxidizing agent) and its corresponding oxidation (or reduction) product; (*iii*) the selectivity of the reaction can be influenced by the applied electrode potential; (*iv*) this method permits the preparation of many substances that cannot be prepared using conventional method.[16] In addition, the particle size of the Cu nanoparticles can be controlled by adjusting the current density.[17-19] This method has been introduced by Reetz and Hilbig[20] in the synthesis of different kind of nanoparticles of different shapes and sizes down to the cluster regime.

Slow-release in the electrochemical synthesis involves the application of applied voltage with a lower value to ensure the the metal ion from the anode slowly releases into the bulk solution. A small size Cu nanoparticles are expected to be produced by using this method. This means that the concentration of metal ions in the bulk solution is low and continuous throughout the synthesis process. In the present study, we focus on the electrochemical synthesis and characterization of Cu(II)St complex. The effect of slow-release synthesis using different values of applied voltages on the particles size and surface morphology of the electrochemically synthesized complex are also investigated in this study.

Experimental

Chemicals

All chemicals used were analytical grade and used without further purification. Stearic acid (HSt) with 99% purity was purchased from Systerm. Cu foil (99% purity) and ethanol (95% purity) was from Sigma-Aldrich. Ammonium acetate (CH_3COONH_4) was purchased from Hamburg chemical GmbH.

Electrochemical synthesis of Cu(II) stearate

The Cu(II)St complex was synthesized using an electrochemical technique. The electrolysis system consisted of a Cu foil (3 × 1 cm, 0.1 cm thickness) as the anode and graphite rod (6.5 mm diameter, Johnson Matthey chemicals Ltd.) as the cathode in the presence of 0.1 mol L^{-1} CH_3COONH_4 as the supporting electrolyte solution. Prior to synthesis, both anode and cathode were rinsed with distilled water and small amount of acetone. A direct current (DC) power supply (TTi PSU Bench CPX400A) was used throughout the electrochemical synthesis. Ethanol was used as the solvent to prepare the 0.1 mol L^{-1} HSt solution. The acid solution was mixed with CH_3COONH_4 solution with the ratio of 1:1 (v/v) into the simple and undivided electrolysis cell (100 mL capacity). The reaction was performed at room temperature (27 °C) for 4 hours.

The resulting complex precipitates as a blue solid in the organic phase and was then separated from the aqueous phase and washed with distilled water and ethanol to remove the impurities. The precipitate was then dried in an oven (50 °C) for 2 hours and allowed to dry at room temperature. To optimize the quality of the synthesized product, several operating parameters were tested such as type of supporting electrolytes, reaction times, applied voltages, and concentrations of supporting electrolyte. The effect of applied voltages on the particle size of the Cu nanoparticles formed and the morphology of the solid Cu(II)St complex conducted using different values of applied voltage (1, 5 and 10 V) is investigated. Analysis of electrochemically synthesized Cu(II)St: mp = 80-85 °C, yield = 99.2%, elemental analysis for $CuC_{36}H_{70}O_4$ (636.21 g mol^{-1}) (calculated): C (67.95%), H (11.99%), O (10.06%), Cu (10.00%); (found): C (67.34%), H (12.20%), O (10.36%), Cu (10.10%).

Instrumentation

The electrochemically synthesized Cu(II)St complex was then characterized using several chemical instruments,

including Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer 1310) in the range of 4000-400 cm^{-1} in KBr pellets, X-ray photoelectron spectroscopy (XPS) (AXIS Ultra 'DLD' by using second edition of Kratos software) and X-ray powder diffraction (XRPD) (Bruker AXS D8 Advance) and the diffraction angle were measured with the X-ray radiation of Cu Kα (40 kV, 40 mA). The concentration of Cu in the aqueous phase solution during the synthesis process was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 4300DV) using 6 series of standard solutions (0.1, 0.3, 0.5, 1.0, 2.0 and 5.0 ppm) as the calibration method, while a CHNS analyzer (Fison EA 1108) was used to determine the elemental composition of the synthesized complex . The melting points were obtained in a capillary tube using an Electrothermal IA9100 melting point apparatus. The size and shape of the nanoparticles were observed using a transmission electron microscopy (TEM) (Philips CM12-12796) with an accelerating voltage of 100 kV. Samples were prepared on carbon-coated copper grids covered with a polyvinyl formal polymer by adding a drop onto the grid and evaporating the solvent (ethanol) in ambient condition. The size values were averaged over more than 120 nanoparticles from different TEM micrographs of the same sample. The surface characterization of Cu(II)St powder was observed by field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDX) (Merlin Compact). Platinum metal was used for sputtering process.

Results and Discussion

Mechanism for the electrochemical synthesis of Cu(II) stearate

The mechanism for the formation of Cu(II)St complex using a electrochemical technique is as follows:

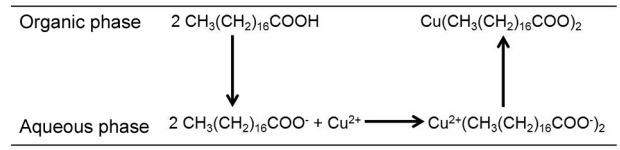
Anode: $Cu^o \rightarrow Cu^{2+} + 2\ e^-$ (1)

Cathode: $2\ e^- + 2\ H_2O \rightarrow H_2 + 2\ OH^-$ (2)

$2\ OH^- + 2\ CH_3(CH_2)_{16}COOH \rightarrow 2\ H_2O + 2\ CH_3(CH_2)_{16}COO^-$ (3)

Overall reaction: $Cu^o + 2\ CH_3(CH_2)_{16}COOH \rightarrow Cu[CH_3(CH_2)_{16}COO]_2 + H_2$ (4)

From the previous mechanism, Cu^{2+} ions (equation 1) were generated in the aqueous phase solution (Scheme 1) at the positively charged anode. At cathode, OH^- ions were generated (equation 2) and directly reacted with HSt to form stearate ion (equation 3) in aqueous phase solution (Scheme 1). The reaction between Cu^{2+} ions and $CH_3(CH_2)_{16}COO^-$ resulted in the formation of Cu(II)St in the organic phase solution (equation 4).



Scheme 1. Mechanism for the electrochemical synthesis of Cu(II)St complex.

Optimization of operating conditions

Optimization of operating conditions were conducted to identify the effect of applied voltage, supporting electrolyte concentration and electrolysis time on the corrosion of Cu anode. Supporting electrolytes are required in electrochemical synthesis to maintain a constant ionic strength, to decrease the resistance of the solution, and to eliminate electromigration effects.[21] Common inorganic salts including sodium chloride (NaCl), potassium nitrate (KNO_3), ammonium chloride (NH_4Cl), and ammonium acetate (CH_3COONH_4) were used as supporting electrolytes due to relatively low costs and high conductivities. The results showed that more Cu^{2+} ions were released from the corroded anode into the aqueous phase of the CH_3COONH_4 supporting electrolyte solution, compared to the other types of supporting electrolytes (Figure 2a). According to Mahoney and Mossaad,[22] CH_3COONH_4 is an acceptable supporting electrolyte material that possesses high conductivity in electrochemical synthesis. Our results confirmed that CH_3COONH_4 provides better conductivity and the highest efficiency in the electrochemical synthesis process.

Electrolysis time is one of the major concerns in chemical synthesis, since longer times may lead to higher energy consumption. In the current study, increases in reaction time generally resulted in increased corrosion of the anode (Figure 2b circle symbol), which produced more Cu^{2+} ions in the aqueous phase solution. For 0.1 mol L^{-1} of HSt, the Cu concentration was generally very low for the first 3 hours due to its use in the formation of the Cu(II)St complex (Figure 2b square symbol). After 3 hours, no more free fatty acid was available in the organic phase and an excess of available Cu^{2+} ions was created in solution. Since unnecessarily long reactions times will result in increased costs due to excess energy consumption and wasted metal species in the aqueous phase, a 4-hour electrolysis time was considered to be the ideal duration to completely react

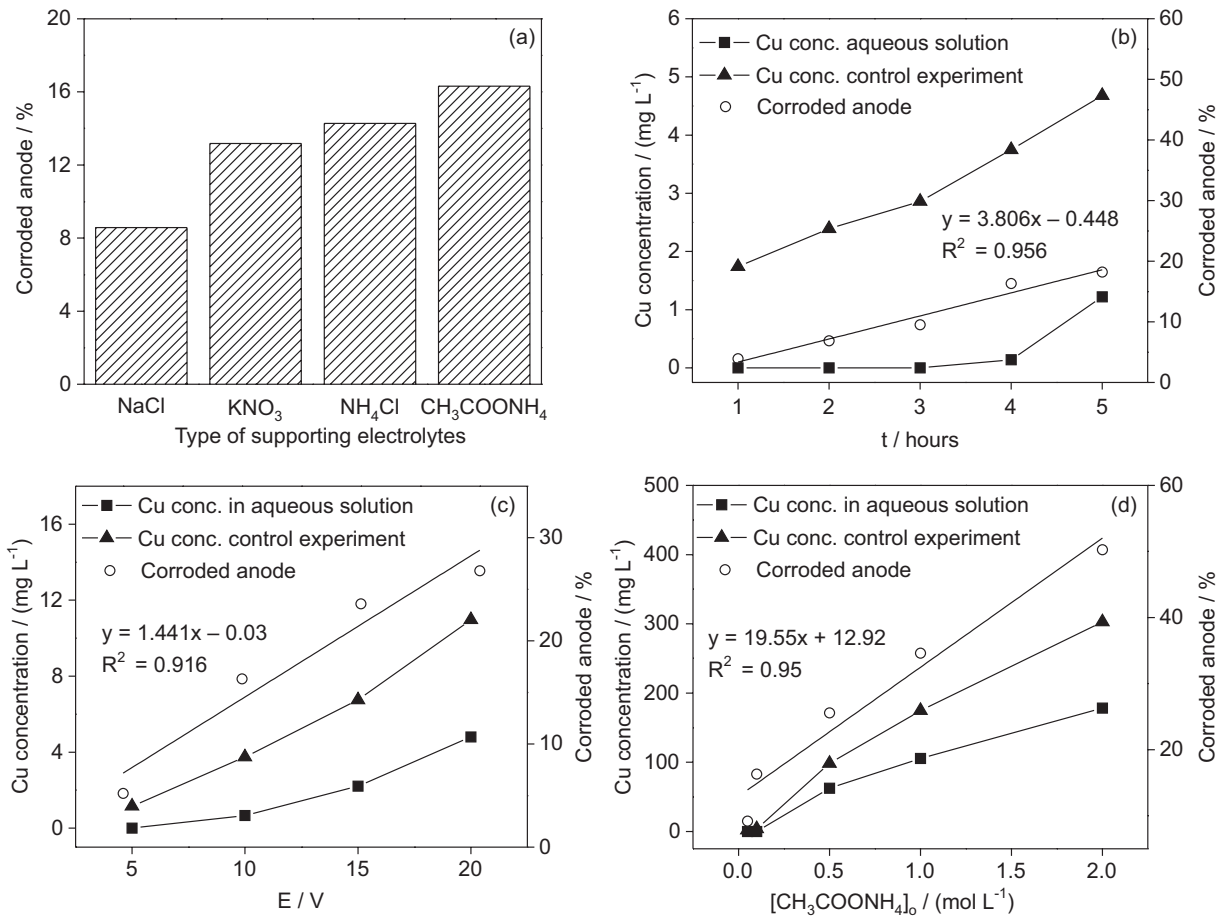


Figure 2. Effects of (a) type of supporting electrolytes; (b) electrolysis times; (c) applied voltages and (d) supporting electrolyte concentrations on percentage of corroded anode (a-d) and Cu^{2+} ion concentration (b-d) in aqueous solution during electrochemical synthesis of Cu(II)St complex. $[HSt]_o$ = 0.1 mol L^{-1} (a-d); [electrolyte] = 0.1 mol L^{-1} (a-c); E = 10 V (a,b and d); t = 4 h (a,c and d).

the fatty acid with Cu^{2+} ions and less wasted Cu species. Electrolysis of CH_3COONH_4 without fatty acids (Figure 2b triangle symbol) was performed as a control experiment to prove that increasing the reaction time produced more Cu^{2+} ions in the aqueous phase solution.

High cell voltages should not be used during electrochemical synthesis to avoid losses of energy, high temperatures, and electrode damage.[23] Selection of the correct supporting electrolyte at an appropriate concentration can assist in minimizing the applied voltage for the electrochemical synthesis process. In the current study, increases in the applied voltage were observed to increase the corrosion percentage of the Cu anode (Figure 2c circle symbol). In the synthesis of Cu(II)St (Figure 2c square symbol), full utilization of fatty acids was achieved with the use of 10 V of applied voltage after 4 hours, without formation of excess Cu^{2+} ions. At 5 V, no excess Cu^{2+} ions formed in solution, but higher concentrations of HSt were still present, and thus the total reaction time at 5 V would possibly be greater than 4 hours. Application of even higher voltages (> 15 V) may reduce the total reaction time but also increase the potential to form certain by-products such as Cu(II) oxides.[22] Therefore, we concluded that 10 V was the ideal applied voltage for the synthesis of Cu(II)St to prevent the formation of undesired compounds.

The main purpose of adding CH_3COONH_4 during the synthesis process is to increase the electrolytic conductivity of the electrochemical system, which in turn affects the current efficiency, cell voltage, and energy consumption in the electrolytic cell.[24] Increasing the concentration of CH_3COONH_4 in the current work was observed to increase the corrosion percentage of Cu anode (Figure 2d circle symbol), which resulted in an increase in the Cu^{2+} concentration. Based on our results, the ideal concentration was 0.1 mol L^{-1} CH_3COONH_4 for 4 hours of reaction time (Figure 2d square symbol). Further increases in CH_3COONH_4 concentration produced excess Cu^{2+} ions. A major drawback of using high concentrations of CH_3COONH_4 (e.g., > 0.5 mol L^{-1}) in the electrochemical synthesis process is heavier cathode plating results.[22] Therefore, we determined that a 0.1 mol L^{-1} CH_3COONH_4 solution was the appropriate concentration of supporting

electrolyte to be used in electrochemical synthesis of Cu(II)St.

Effect of applied voltages on the synthesis of Cu(II) stearate complex

Figure 3 shows the effect of different applied voltages on current and resistance during the electrochemical synthesis of Cu(II)St complex for 60 min. According to Ohm's law (voltage = current × resistance), voltage is directly proportional to the generated current (I). The value of $I_{t=0}$ (21.72 mA) in Figure 3a using 10 V of the applied voltage is the highest compared to other applied voltages (10.70 mA for 5 V (Figure 3b) and 1.36 mA for 1 V (Figure 3c)). This shows that the use of high voltage will directly increase current flows and thus increase the Cu anode corrosion to produce more Cu ions for complex formation. This result was in line with the result explained in Figure 2c.

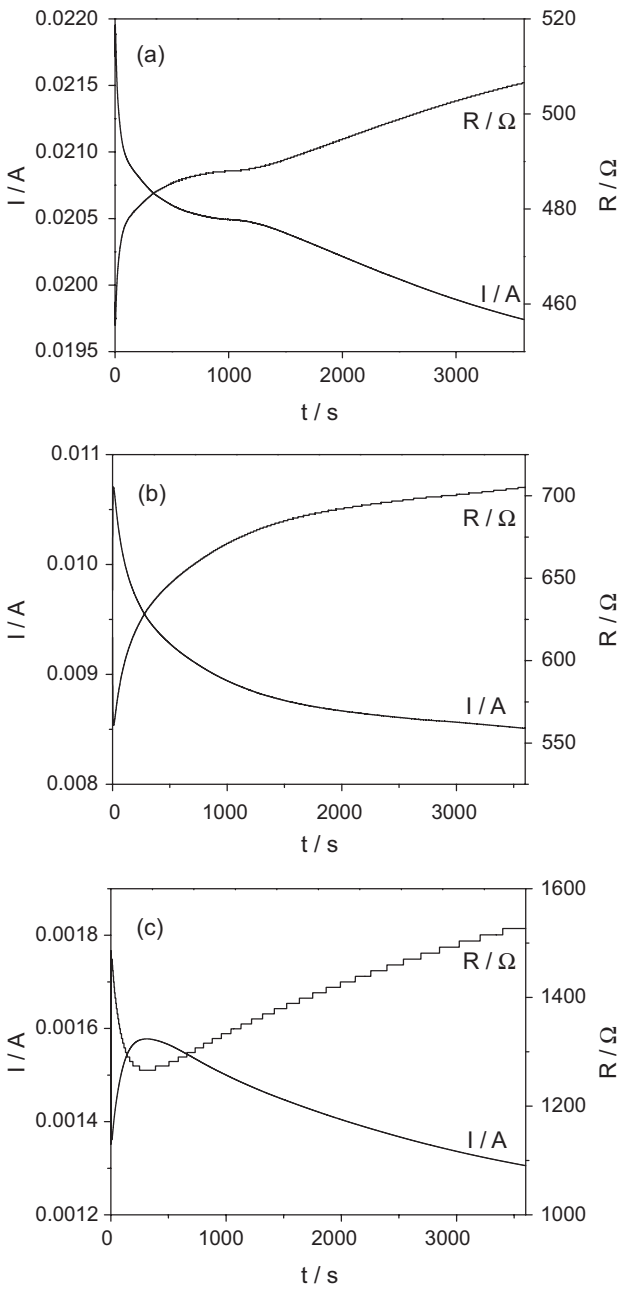


Figure 3. Effects of applied voltages on resulting current and resistance in the synthesis of Cu(II)St complexes using (a) 10 V; (b) 5 V and (c) 1 V of applied voltage. $[HSt]_o$ = 0.1 mol L^{-1}; $[CH_3COONH_4]$ = 0.1 mol L^{-1}; t = 60 min; T = room temperature (27 °C); stirring speed: 1000 rpm.

Graph of I *vs.* t in Figure 3c is different from the others in which there is a current "spike" during the first 6 minutes of the synthesis process ($I_{t=0}$ = 1.36 mA; $I_{t=6min}$ = 1.58 mA). The application of 1 V of applied voltage during the synthesis reduces the generated Cu^{2+} ions in the bulk solution thus slows the rate of complex formation. Therefore, 6 minutes are required to produce sufficient concentration of Cu^{2+} ions to initiate the Cu(II)St formation. After 6 minutes, the graph shows a gradual decay in the current until the end of the electrolysis. Graph of R *vs.* t in Figure 3c shows that after 6 min, the resistance (Ω value) was increased towards the end of the electrolysis. This is due to the continuous production of Cu^{2+} ions in the solution and causing the increase of complex formation. The Cu(II)St complex produced is not electricity conductor, resulting in a decrease in current flows, while the resistance is increasing. In contrast with the synthesis using 10 and 5 V of applied voltages (Figures 3a and 3b), there is a gradual decay in the current while increasing the resistance from the beginning until the end of the reaction time. This demonstrates the ability of these applied voltages to produce a higher concentration of Cu^{2+} ions which is sufficient to initiate the complex formation and increase the rate of complex formation.

The effect of applied voltages on the generation of Cu^{2+} ions concentration in aqueous phase solution was studied using Faraday equation based on the data obtained in Figure 3. Faraday equation is as follows:

$$m = {}^{AQ}\!/_{zF} \quad (5)$$

where m = mass of dissolved Cu (g); A = relative atomic mass (g mol^{-1}); Q = charge (C); z = number of charges; and F = Faraday constant (96 485 C mol^{-1}). Table 1 (calculated) shows the mass of dissolved Cu in solution after 60 min of electrolysis was highest using 10 V of applied voltage, followed by 5 V and 1 V. These results are in accordance with the conclusions of the results from Figure 3 and 2c, in which the increase of applied voltage increases the corrosion of Cu anode. To support the results obtained in Table 1 (calculated), Cu anode was weighed before and after electrolysis to determine the mass of corroded

anode. The results obtained are summarized in Table 1 (found). The mass of corroded anode that we found in this experiment is not that different from the calculated ones using Faraday equation. Therefore, we can conclude there are no significant differences from the result obtained in this study with the calculated value.

Table 1. Mass of dissolved Cu (calculated and found)

Applied voltage / V	Mass of dissolved Cu (calculated)[a] / g	Mass of corroded Cu anode (found) / g
1	$0.001 \pm 1.015 \times 10^{-4}$	0.002 ± 0.002
5	0.010 ± 0.001	0.008 ± 0.001
10	$0.022 \pm 7.071 \times 10^{-4}$	0.020 ± 0.003

Data are expressed as mean ± SD; [a]calculated using Faraday equation.

Characterization of electrochemically synthesized Cu(II) stearate

A peak at 1697 cm^{-1} was observed on the IR spectrum of HSt (Supplementary Information, Figure S1), and this was assigned to the stretching vibration of the carboxylate group of HSt.[1] For both spectra, the presence of peaks at wavenumbers 2800-3000 cm^{-1} represented the asymmetric (v_{as}) and symmetric (v_s) stretching vibrations of the methyl and methylene groups of fatty acid ligands.[6] The asymmetric and symmetric stretching vibrations of the coordinate carboxylate groups appeared at 1589 and 1424 cm^{-1}, respectively. These bands are characteristic of dicopper tetracarboxylate complexes.[6]

Several authors[6-8] have proposed that the positions of asymmetric (v_{as}) and symmetric (v_s) stretching vibrations of carboxylate groups ($\Delta v_{COO} = v_{COO,as} - v_{COO,s}$) can be used to distinguish the type of carboxylate-to-metal complexation structure of Cu(II) carboxylates. A value of Δv_{COO} in the range of 150-170 cm^{-1} corresponds to a bridging bidentate Cu(II) coordination, while $\Delta v_{COO} > 200$ cm^{-1} is an indication for complexes with monodentate carboxylic groups.[8] In the IR spectrum in Figure S1, $v_{COO,as}$ = 1588 cm^{-1} while $v_{COO,s}$ = 1421 cm^{-1}, giving the value of Δv_{COO} = 167 cm^{-1}. This value corresponded to a bridging bidentate mode of coordination and was in agreement with the results from previous studies. This proved that the desired complex have been synthesized.

From the XPS spectrum in (Supplementary Information, Figure S2a), the synthesized complex was composed of C, O and Cu element. The content of carbon is very high (about 69.48%) compared to other elements due to the presence of carbon chain of HSt. The binding energies were referenced to the C1s line at 284.5 eV from adventitious carbon. Deconvolution of C1s peaks showed the existence of different carbon species in the electrochemically synthesized Cu(II)St complex. The XPS spectrum of C1s (Supplementary Information, Figure S2b) shows that there are three types of carbon in the synthesized complex which are fitted to the –C=O (288.2 eV) and –C–C (285.5 eV) while peak at 284.5 eV corresponds to carbon of HSt chain (–C–H).[25]

The XRPD patterns of HSt and Cu(II)St (Supplementary Information, Figure S3) were verified by comparison to the HSt file (JCPDS No. 04-0364) and Cu(II)St file (JCPDS No. 55-1622). Well-defined diffraction peaks were observed for both patterns, and thus both of the samples crystallized into layered structures. The peak cluster between 15-20° in the patterns of Cu(II)St has been reported for HSt.[26] These cluster peaks for HSt are slightly shifted to a lower angle after complex formation. The peak at low angles 1.76° for HSt was shifted to a lower angle (1.57°) after formation of Cu(II)St. This result proved that crystal formation occurred between Cu^{2+} ions and HSt ligands.

Particle size analysis

A TEM micrographs obtained for Cu samples shows the presence of small Cu clusters forming aggregates of different size (Figure 4). The micrograph in Figure 4a shows the formation of small size particles in the range of 1-3 nm with an average particle size of 2.49 ± 0.82 nm during the synthesis of Cu(II)St using 1 V of applied voltage. In contrast to the synthesis using 5 and 10 V (Figures 4b and 4c), the particles formed are bigger in size with an average particle size are 3.61 ± 1.18 nm and 6.64 ± 2.72 nm respectively. This indicates that the particle size of the synthesized product can be controlled by adjusting the applied voltage during the synthesis process as was reported by several researchers.[27,28]

Application of high applied voltage (i.e., 10 V) during the synthesis increases the generation of Cu particles in the bulk solution. Consequently, the particles have a tendency to agglomerate and being traps within the ligand used and resulting in larger particle size.[27] In Figure 4a, fewer particles are agglomerate as a result of less generation of Cu particles in the synthesis using 1 V. This is the advantage of slow-release electrochemical synthesis using lower applied voltage (i.e., 1 V) in which the Cu ion generated from the Cu anode are slowly released into the bulk solution containing HSt. Thus, less agglomeration occurred and small particles size of the metal is obtained.

Surface morphology analysis

Based on the FESEM micrographs, the electrochemically synthesized Cu(II)St complexes formed petal-like

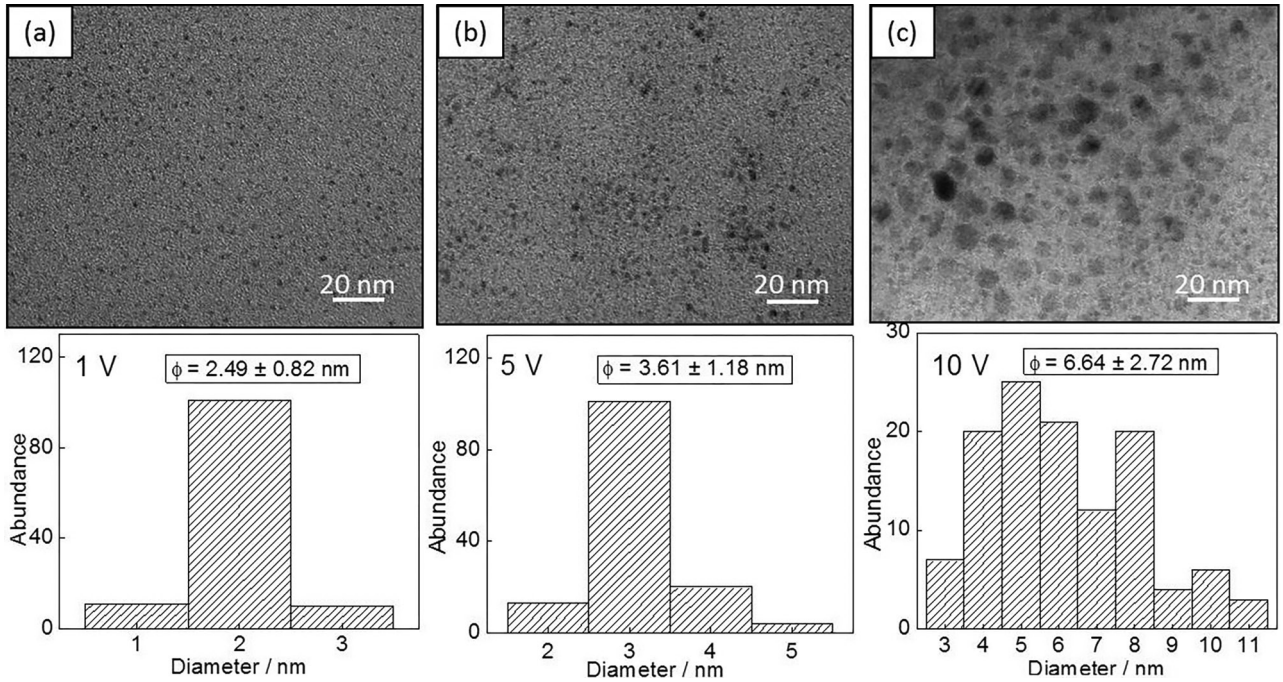
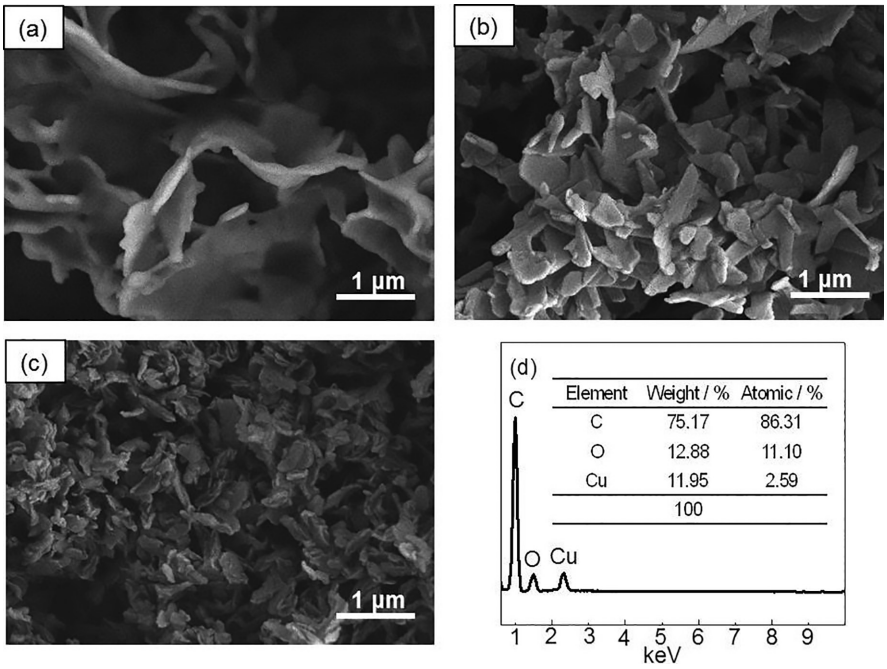


Figure 4. TEM images and size distribution of Cu nanoparticles synthesized using (a) 1 V; (b) 5 V; and (c) 10 V of applied voltage; magnification = 160000×.

structures (Figure 5). This result is in accordance with other results already reported in the literature.[1,2] The synthesis of Cu(II)St complex using different values of applied voltages produces different size of Cu(II)St complex cluster. Figure 5a shows that by using 1 V of applied voltage, the cluster formed are larger in size, followed by 5 V (Figure 5b) and 10 V (Figure 5c). The cluster formed using high applied voltage (10 V) seems to be broken into small pieces as in Figure 5c. Consequently, the cluster size of the complex is smaller than Figure 5b followed by Figure 5a. This might be the consequence of consumption of high applied voltage as it inhibits the formation of a well-shaped petal-like structure. EDX analysis was performed to determine the distribution of elements on the surface of



Element	Weight / %	Atomic / %
C	75.17	86.31
O	12.88	11.10
Cu	11.95	2.59
	100	

Figure 5. FESEM micrograph of synthesized Cu(II)St with 20000× magnification using (a) 1 V; (b) 5 V; (c) 10 V of applied voltage and (d) EDX spectrum of electrochemically synthesized Cu(II)St.

the complex. The result obtained in Figure 5d proved that the synthesized complex composed of C, O and Cu. This result was in line with the result obtained by XPS analysis in Figure S2a (Supplementary Information).

Conclusions

The release of Cu^{2+} ions into the aqueous solution depends on the type and concentration of supporting electrolytes, reaction times, and applied voltages. Ammonium acetate (CH_3COONH_4) was determined to be the best supporting electrolyte in the electrochemical synthesis of Cu(II)St complex. Meanwhile, increases in the reaction time, applied voltage, and concentration of CH_3COONH_4 resulted in the increased concentration of Cu^{2+} ions in the aqueous phase solution, and thus enhanced the efficiency of the complex formation and reduced the energy consumption. The characterization using FTIR, XPS and XRPD proved that the synthesized complex was the desired Cu(II)St complex. The results from spectroscopic studies using FTIR and XPS confirm the presence of bonding between the coordinated carboxylate group of HSt with Cu^{2+} ions. To study the effect of applied voltages on the particle size of the Cu nanoparticles produced, the applied voltage of the electrolysis process was varied which is 1, 5 and 10 V. The particle size analysis using TEM showed that the synthesis using 1 V of applied voltage produces small Cu cluster with an average particle size of 2.49 ± 0.82 nm while by using 5 V and 10 V, the resulting Cu cluster are much bigger in size which is 3.61 ± 1.18 nm and 6.64 ± 2.72 nm, respectively. In addition, the synthesis using 1 V of applied voltage formed petal-like structure whereas higher values of the applied voltage inhibit the formation of well-shaped petal-like structure. This proves that the small Cu cluster was successfully obtained in the slow-release electrochemical synthesis of Cu(II)St complex using 1 V of applied voltage. The results of this study can potentially be used to investigate the synthesis of other divalent metal complexes of interest to chemistry, biochemistry and industry.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

The funding from Universiti Kebangsaan Malaysia through grants AP/2012/017, DLP-2013-002 and DPP-2013-045 are gratefully acknowledged. We wish to express special thanks to Ministry of Education of Malaysia for postgraduate scholarship (MyBrain15) and Centre for Research & Instrumentation Management (CRIM), UKM for XRPD, XPS and FESEM analyses.

References

1. Chen, L.; Meng, H.; Jiang, L.; Wang, S.; *Chem. - Asian J.* **2011**, *6*, 1757.
2. Wang, S.; Feng, L.; Jiang, L.; *Adv. Mater.* **2006**, *18*, 767.
3. Papaefstathiou, G. S.; MacGillivray, L. R.; *Coord. Chem. Rev.* **2003**, *246*, 169.
4. Mao, G.; Dong, W.; Kurth, D. G.; Mohwald, H.; *Nano Lett.* **2004**, *4*, 249.
5. Kozlevcar, B.; Lah, N.; Makuc, S.; Segedin, P.; *Acta Chim. Slov.* **2000**, *47*, 421.
6. Doyle, A.; Felcman, J.; Teresa, M.; Braganc, M. L.; *Polyhedron* **2000**, *19*, 2621.
7. Iqbal, M.; Ali, S.; Muhammad, N.; Sohail, M.; *Polyhedron* **2013**, *57*, 83.
8. Wojciechowski, K.; Bitner, A.; Bernardinelli, G.; Brynda, M.; *Dalton Trans.* **2009**, *7*, 1114.
9. Vaughan, G. B. M.; Sghmidt, S.; Poulsen, H. F.; *Z. Kristallogr.* **2004**, *219*, 813.
10. Kozlevcar, B.; Leban, I.; Petric, M.; Petricek, S.; Roubeau, O.; Reedijk, J.; Segedin, P.; *Inorg. Chim. Acta* **2004**, *357*, 4220.
11. Jaskova, J.; Miklos, D.; Korabik, M.; Jorik, V.; Segl'a, P.; Kalinakova, B.; Hudecova, D.; Svorec, J.; Fischer, A.; Mrozinski, J.; Lis, T.; Melnik, M.; *Inorg. Chim. Acta* **2007**, *360*, 2711.
12. Goto, M.; Kani, Y.; Tsuchimoto, M.; Ohba, S.; Matsushima, H.; Tokii, T.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 7.
13. Wojciechowski, K.; Kucharek, M.; Buffle, J.; *J. Membr. Sci.* **2008**, *314*, 152.
14. Ramos Riesco, M.; Martınez Casado, F. J.; Lopez-Andres, S.; Garcıa Perez, M. V.; Redondo Yelamos, M. I.; Torres, M. R.; Garrido, L.; Rodrıguez Cheda, J. A.; *Cryst. Growth Des.* **2008**, *8*, 2547.
15. Ramos Moita, M. F.; Duarte, M. L. T. S.; Fausto, R.; *Spectrosc. Lett*. **1994**, *27*, 1421.
16. Jolly, W. L.; *The Synthesis and Characterization of Inorganic Compounds*, 1st ed.; Prentice-Hall: New Jersey, 1970.
17. Rodriguez-Sanchez, L.; Blanco, M. C.; Lopez-Quintela, M. A.; *J. Phys. Chem. B* **2000**, *104*, 9683.
18. Khaydarov, R. A.; Khaydarov, R. R.; Gapurova, O.; Estrin, Y.; Scheper, T.; *J. Nanopart. Res.* **2009**, *11*, 1193.
19. Vilar-Vidal, N.; Blanco, M. C.; Lopez-Quintela, M. A.; Rivas, J.; Serra, C.; *J. Phys. Chem. C* **2010**, *114*, 15924.
20. Reetz, M. T.; Helbig, W.; *J. Am. Chem. Soc.* **1994**, *116*, 7401.
21. Plambeck, J. A.; *Electroanalytical Chemistry: Basic Principles and Applications,* 2nd ed.; Wiley: New York, 1982.

22. Mahoney, D. M.; Mossaad, G. S.; *US pat. 5,443,698* **1995**.
23. Sakalis, A.; Fytianos, K.; Nickel, U.; Voulgaropoulos, A.; *Chem. Eng. J.* **2006**, *119*, 127.
24. Sengil, I. A.; Ozacar, M.; *J. Hazard. Mater*. **2009**, *161*, 1369
25. Deng, D.; Qi, T.; Cheng, Y.; Jin, Y.; Xiao, F.; *J. Mater. Sci.: Mater. Electron*. **2014**, *25*, 390.
26. Corbeil, M. C.; Robinet, L.; *Powder Diffr*. **2002**, *17*, 52.
27. Saito, G.; Wan Mohd Azman, W. O. S.; Nakasugi, Y.; Akiyama, T.; *Adv. Powder Technol.* **2014**, *25*, 1038.
28. Long, Y. M.; Zhao, Q. L.; Zhang, Z. L.; Tian, Z. Q.; Pang, D. W.; *Analyst* **2012**, *134*, 805.

Submitted: November 28, 2014
Published online: March 27, 2015