# The Morphology of Micro Crystals of Copper Metal and Copper (I) Oxide Synthesized in the Presence of a Shape Controlling Agent

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## Abstract

This work aims to observe the effect of pH on the composition and morphology of the products synthesized with the support of a shape controlling agent. A series of the mild condition at 40°C synthesis was conducted using copper (II) sulfate and ascorbic acid as the starting reagent over the pH range of 3-10. Nonionic surfactant polyoxyethylene nonylphenyl ether (n=9) (PONPE-9) was employed as the shape controlling agent. All products were washed with distilled water and ethanol, filtered and dried before subjected to characterize using SEM, XRD, and TEM. It was found that the products obtained under the different pH could be classified into two groups. The first group obtained from pH 3-4 was pure metal Cu with diversity rod-like morphologies. The second group obtained from pH 5-10 had the high distribution size of hollow sphere copper (I) oxide microparticles. The different morphologies between two groups suggested the role of hydroxide ion at the concentration above $K_{sp}$ of the hydroxo copper (II) complex. The role of PONPE-9 was also ascribed and proposed the scheme of how to control the growth of the crystal, both pure copper and copper (I) oxide, with different mechanisms.

***Keywords*: *Copper metal, Copper (I) oxide*, *PONPE, hollow sphere***

## บทคัดย่อ

งานวิจัยนี้มีเป้าหมายเพื่อศึกษาผลของ pH ต่อองค์ประกอบและรูปร่างของผลิตภัณฑ์เมื่อใช้สารควบคุมรูปร่างในปฏิกิริยา **วิธีดำเนินการวิจัย** สังเคราะห์ที่ค่า pH 3-10 ที่อุณหภูมิ 40 องศาเซลเซียส โดยใช้ทองแดง (II) ซัลเฟต และกรดแอสคอร์บิกเป็นสารตั้งต้น ใช้สารลดแรงตึงผิวโพลิออกซีเอทิลีน โนนิล เฟนนิล (n=9) (PONPE-9) เป็นสารควบคุมรูปร่าง ล้างตะกอนที่ได้ด้วยน้ำกลั่นและเอทานอล ทำให้แห้ง แล้วตรวจสอบสมบัติต่าง ๆ ด้วยเครื่อง SEM, XRD, และ TEM. ผลการทดลองพบว่ารูปร่างของผลิตภัณฑ์ที่ pH ต่าง ๆ สามารถจำแนกได้เป็น 2 กลุ่ม กลุ่มแรกที่สังเคราะห์ที่ pH 3-4 จะได้ผลิตภัณฑ์เป็นโลหะทองแดงบริสุทธิ์ที่มีรูปทรงส่วนใหญ่เป็นแท่งขนาดต่าง ๆ ในขณะที่ผลิตภัณฑ์ที่ pH ช่วง 5-10 จะเป็นสารประกอบทองแดง (I) ออกไซด์ ที่เป็นทรงกลมกลวงขนาดไมโครเมตร ความเข้มข้นของไฮดรอกไซด์ไอออน มีผลต่อองค์ประกอบของผลิตภัณฑ์ โดยถ้าไฮดรอกไซด์ไอออนเข้มข้นมากกว่าที่สภาวะสมดุลของ Ksp ของสารประกอบไฮดรอกโซ ทองแดง (II) จะได้สารประกอบเป็นทองแดง (I) ออกไซด์ นอกจากนั้นงานวิจัยนี้ได้เสนอกลไกและบทบาทของ PONPE-9 ที่มีผลต่อรูปร่างของผลิตภัณฑ์ทั้งสองกลุ่ม โดยพบว่า PONPE-9 ควบคุมรูปร่างด้วยกลไกที่แตกต่างกัน

**คำสำคัญ :** *โลหะทองแดง ทองแดง* (I)*ออกไซด์* PONPE *ทรงกลมกลวง*

## 1. Introduction

From our previous work, we demonstrated the method to produce copper (I) oxide hollow sphere particle with the support of nonionic surfactant, polyoxyethylene nonyl phenyl ether (n=9) (PONPE-9), at pH 7 (Wongwailikhit & Sripoomwattana, 2013). The process can be succeeded within one pot synthesis at 40°C using $CuSO_4$ and ascorbic acid as the starting reagents. PONPE-9 was found to be the excellent shape controlling agent because the self-assembly of hollow sphere copper (I) oxide could be formed within only 30 minutes. It should be claimed here that our process is a quite simple and promising scale-up method compared to some procedures which suffered from the use of high temperature (Sui et al., 2009; Cao et al., 2010; Zhang, 2007). Moreover, the hollow structure with high surface area of $Cu_2O$ has spurred great interest owing to its potential catalyst for many organic syntheses (White et al., 2006) and some promising applications for photoconductivity materials (Wang et al., 2014; Xu, Wang & Zhou, 2008; Gao et al., 2008; Zhou et al., 2014). Then, it is worthy to study deeply the synthetic conditions used to achieve certain morphologies. The outcome may not only provide insights into factors controlling the particle morphology but also enable the feasibility to develop the potential industrial procedures of the synthesis process.

In this study, we focus our attention on the effect of pH on the product composition and morphology. The pH of the mixtures between $CuSO_4$ and PONPE-9 was adjusted in the range of 3-10 before adding a reducing agent, ascorbic acid. The products were characterized using some spectrophotometry including SEM and TEM. We demonstrated the method to produce copper (I) oxide hollow sphere particle with the support of nonionic surfactant, polyoxyethylene nonyl phenyl ether (n=9) (PONPE-9), at pH 7 (Wongwailikhit & Sripoomwattana, 2013).

## 2. Objectives

This work studied the effect of pH on the composition and morphology of the products synthesized with the support of a nonionic surfactant, polyethylene nonyl phenyl ether (n=9) (PONPE-9).

## 3. Materials and Methods

### 3.1 Materials

Copper sulfate pentahydrate and ascorbic acid were of analytical grade purchased from J.T.Baker Co. Ltd. polyoxyethylene (9) nonylphenyl ether (PONPE-9) was purchased from Aldrich chemicals. All surfactants were used without purification. The absolute ethanol (HPLC grade) solvent was from Mallinckrodt chemicals. All reagents were used as received. Water was double deionized and distilled.

### 3.2 Methods

A set of experiments was conducted by mixing an aliquot of 10 mL of 50 mmolal of surfactant with 1 mL of 0.5 M $CuSO_4$. The pH of a solution was adjusted as designed with 0.1 M $H_2SO_4$ or 0.1 M NaOH. Then add 250 microliters of 1.0 M ascorbic acid. The mixed solution was then subjected to a temperature controllable sonicator for 2 hours. Temperature was kept at 40 °C. After that, wash the precipitate with distilled water for many times and clean the precipitate with absolute ethanol. Finally, dry the precipitate overnight at 100°C.

The morphologies and sample size of the products were examined using a scanning electron microscope: SEM (JEOL model JSM 6301-F) mounted with Electron Dispersion Spectroscopy (EDS). The phase and the crystallographic structure of the products were characterized by X-ray diffraction analysis (X-Ray Diffractometer: Bruker AXS, Model D8 Advance) using Cu $K_\alpha$ at 40 kV, 30 mA and 1.54056 A°. The transmission electron microscope (TEM) images were obtained by a Hitachi Model H-800 operating at the accelerating voltage of 200 kV.

## 4. Results

### 4.1 Effects of pH

Products synthesized over a range of pH 3-10 were first analyzed via SEM. It was found that morphologies of the product could be grouped into two main morphologies. Details of each group were described separately as follows. .

4.1.1 Products with geometrical shapes.

The first group was obtained at pH 3-4 where the irregular geometrical shapes such as rods, triangles, including the unidentified shapes were found. Rod shapes with various aspect ratios were the majority as shown in Figure 1.

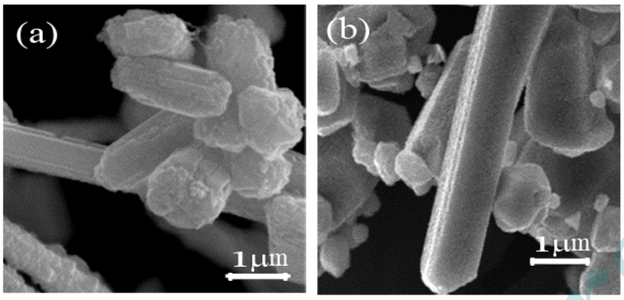

**Figure 1** SEM of products obtained at pH 3-4 and 40$^o$C in the vicinity of PONPE-9 (a) pH 3 (b) pH 4

Figure 1 shows the SEM images of products prepared at pH 3-4 under different PONPEs. It was clearly shown that the products were diversity in size and shape. The majority of morphology was the imperfect rod-like shape with various aspect ratios. The preferential rod shape suggested the different crystal grown rate against the specific facet of the crystal. More information was required for further discussion so crystalline product obtained from pH 3 was subjected as a representative of this group to analyze further using EDS and XRD. The results were detailed later on.

4.1.2 Products with spherical hollow morphologies

The second group performed spherical products with rough surface. Those were obtained from a wide range of pH 5-10. SEM images of products yielded from pH 5-10 were shown in Figure 2.

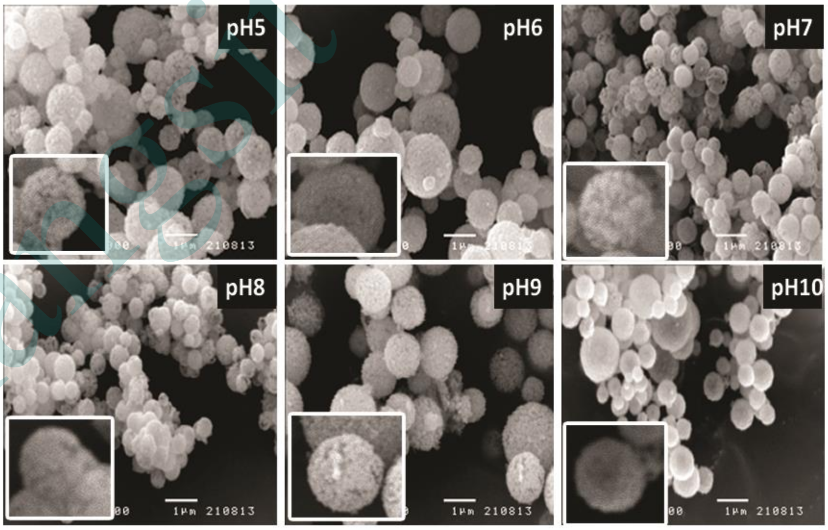

**Figure 2** SEM of products obtained at pH 5-10 and 40$^o$C in the vicinity of PONPE-9.

All products of this group showed spherical shapes with different sizes as shown in Figure 2. Some particles were broken which clearly find the hollow structure for all products (shown in the insets ). It could be seen from the SEM images that the rough surface of the sphere was made up of small particles ascending along the surface of the sphere. The incomplete joining between small particles left some voids on the surface of the spheres. A sample of the products in this group was subjected to analyze the composition further with the same method of group 1.

To elucidate the chemical structure for those products, the products obtained at pH 7 with PONPE-9 were chosen and analyzed for the chemical composition using EDS and XRD. The results were depicted in Figure 3.

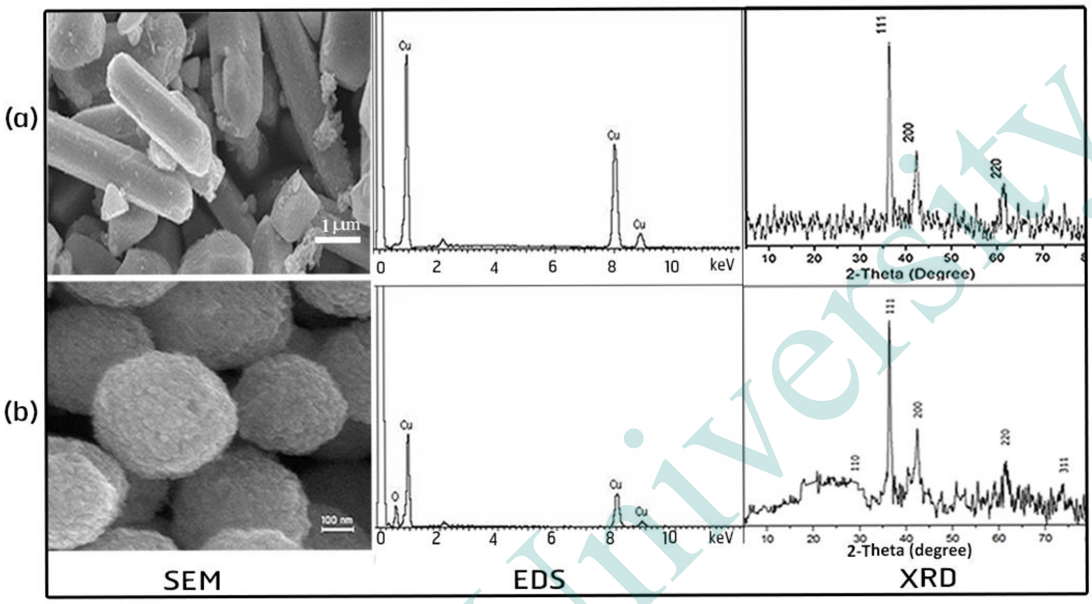

**Figure 3** SEM, EDS and XRD of product obtained at (a) pH 3 and (b) pH 7

Figure 3 illustrated the corresponding SEM, EDS spectra and XRD diffraction for both products at pH 3 (Figure 3a) and pH 7 (Figure 3b), respectively. Figure 3a showed the EDS absorption peaks of only Cu metal from product at pH 3 which suggested the purity of the copper metal obtained. The X-ray diffraction peaks of this product at $2\theta$ were assigned to be [111], [200], and [220] for pure copper with respect to JCPDS No: 85-1326. Both observations confirmed that the product yielded from pH 3 was pure copper.

Figure 3b showed the EDS spectrum of product from pH 7, and it was found that the oxygen adsorption peaks including Cu metal peaks represented the copper oxide formation which is probably CuO or $Cu_2O$. However, the XRD diffraction pattern which assigned peaks [111], [200], [220], and [311] planes was in agreement with general pattern of $Cu_2O$ (JCPDS No: 78-2076). Hence, the hollow spherical products obtained from pH 7 were $Cu_2O$. Moreover, these results agreed well with ones of the previous work reporting on Cu and $Cu_2O$ nanoparticles (Chen, Chiang & Wu, 2012). Then, we made the reasonable conclusion that the first group of products obtained from pH 3-4 was pure copper metal while the other was $Cu_2O$ nanoparticles.

## 5. Discussion

The distinction products between two groups concerned the different reaction pathways between groups which was attributed to the difference in hydroxide concentration. This section was attempted to describe the grown mechanism of Cu and $Cu_2O$ produced particularly by the self assembly of hollow sphere under the support of PONPE as follows.

### 5.1 Basic Chemistry of Cu and $Cu_2O$ formation.

First, basic mechanism of Cu and $Cu_2O$ formation in aqueous solution without PONPE was explained as follows. Copper (II) ion ($Cu^{2+}$) exists in water with octahedral structure of hexaaqua copper (II) ion of $[Cu(H_2O)_6]^{2+}$ (aq). In acidic solution, $Cu^{2+}$ in $[Cu(H_2O)_6]^{2+}$ is reduced to form $Cu^o$ by gaining 2 electrons from the reducing agent as in the equation (5.1).

$$Cu^{2+}\,(aq) + 2e^- \longrightarrow Cu^o\,(s) \qquad (5.1)$$

When sodium hydroxide is added to hexaaqua copper (II) ion solution, $OH^-$ can predominantly displace $H_2O$ ligand and form dihydroxotetraaquo copper (II) complex, $[Cu(OH)_2(H_2O)_4]$, which is identical to $Cu(OH)_2$ as in the equation 5.2.

$$[Cu(H_2O)_6]^{2+}\,(aq) + 2OH^-\,(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4]\,(s) + 2H_2O\,(l) \qquad (5.2)$$

$$[Cu(OH)_2(H_2O)_4]\,(s) = Cu(OH)_2\,(s)$$

Equation 5.2 can be written more simply as in equation 5.3.

$$Cu^{2+}\,(aq) + 2OH^-\,(aq) \rightleftharpoons Cu(OH)_2\,(s) \qquad (5.3)$$

$[Cu(H_2O)_4(OH)_2]$ (s) is likely to precipitate because of its low solubility in aqueous solution. However, in strong alkaline solutions, the ligand displacement reaction can be further incorporated and tetrahydroxocuprate(II) complex anion is formed as in the equation 5.4 (Doc Brown's Chemistry, the chemistry of copper, online).

$$Cu(OH)_2\,(s) + 2OH^-\,(aq) \rightleftharpoons [Cu(OH)_4(H_2O)_2]^{2-}\,(aq) \qquad (5.4)$$

To be more precise, if $Cu(OH)_2$ (s) is written as $[Cu(H_2O)_4(OH)_2]$(s), the equation 5.4 can be rewritten as:

$$[Cu(OH)_2(H_2O)_4]\,(s) + 2OH^-\,(aq) \rightleftharpoons [Cu(OH)_4(H_2O)_2]^{2-}\,(aq) + 2H_2O\,(l) \qquad (5.5)$$

After a reducing agent is added, $Cu(OH)_2$(aq) is reduced from $Cu^{2+}$ to $Cu^+$ (aq) in $Cu_2O$ (s).

$$2Cu(OH)_2 + e- \rightleftharpoons \tfrac{1}{2}\,Cu_2O + 2H_2O \qquad (5.6)$$

5.2 Pathway of copper metal and growth of rod morphology

At pH 3-4, it was described that the concentration of $OH^-$ was too low to coordinate with copper (II) ion in $[Cu(H_2O)_6]^{2+}$. The redox reaction undertaken with ascorbic acid as the reducing agent was shown in equation 5.7 (Zhang et al., 2007).

$$C_6H_8O_6\,(aq) + Cu^{2+}(aq) \rightarrow C_6H_6O_6\,(aq) + Cu^{o}\,(s) + 2H^+ \qquad (5.7)$$

The obtained copper metal was formed with 3D expansion and showed majority in rod-like shape (Figure 1) with different aspect ratios. The difference in the growth rate against facet plane was attributed to the selectivity of PONPE adsorption on the crystal facet to be described later on. To illustrate the role of PONPE in shaping the product, a set of the experiments synthesized with and without PONPE was conducted and the results were shown in Figure 4.

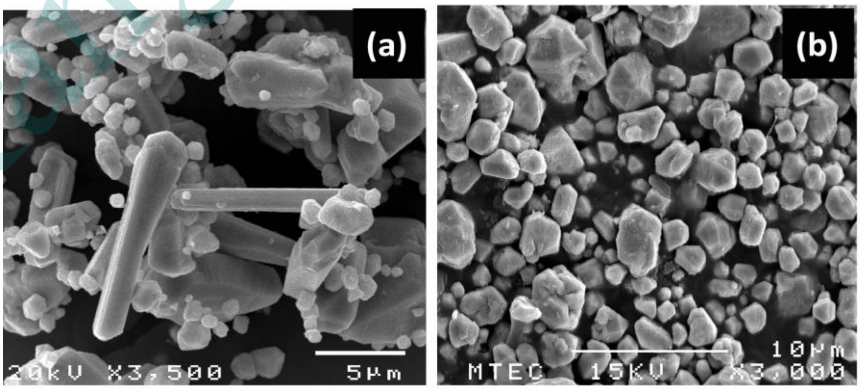

**Figure 4** SEM of the products yielded from the synthesis of pH 3 at 40 °C (a) with PONPE-9 (b) without PONPE-9

It was clearly elucidated in Figure 4 that crystal obtained from pH 3 with PONPE (Figure 5(a)) performed the anisotropic propagation of the products over than that without PONPE (Figure 5(b)). The presence of PONPE in the synthetic reaction can shape the metal product in the same way as other surfactants such as CTAB studied by Xia et al. (2009), Cao et al. (2003), and De & Mandal (2013), or

Triton X-114 studied by Lui, Liu & Jiang (2010). PONPE was claimed as the capping agent and able to change the order of free energies of the crystal planes and to provide the different growth rates at the specific planes (Xia et al., 2009; Lisiecki, 2005). Polyethylene oxide groups of non-ionic surfactant were preferentially passivated onto the {100} facet planes of fcc metal more than those of {111}. It was attributed to the distinction of atomic densities between facets (Tiberg, Brinck & Grant, 2000; Jaschke et al., 1997; Paria & Khilar, 2004). The facet {100} has lower atomic density and more open sites for the adsorption of surfactants, rendering nanoparticles capable of attaching toward the less covered {111} to propagate more in one direction as shown in Figure 5

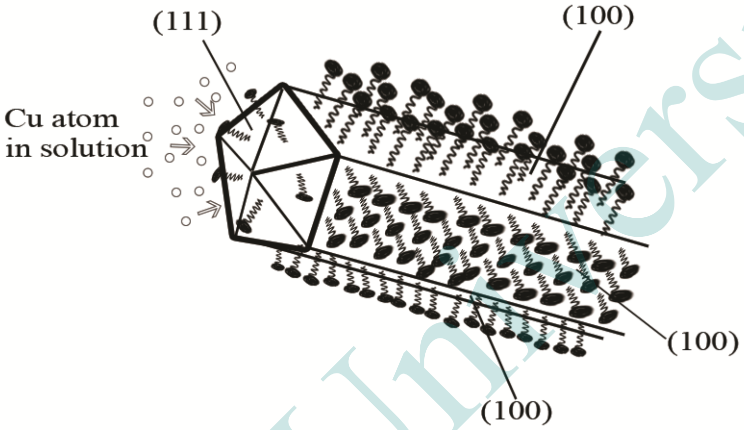

**Figure 5** The preferential adsorption of PONPE to the lateral {100} facet of copper rod. Growth of copper rod was succeeded by accommodating copper atoms to the end (111) facets.

Figure 5 is a drawing picture illustrating the adsorption of surfactants onto the {100} facet and the growth of crystal toward the {111} facet (Bakshi, 2016) to form rod-like and wire shapes (Lui, Liu & Jiang, 2010; Xia et al., 2009).

5.3 The self-assembly conformation of copper (I) oxide hollow sphere in the presence of PONPE

As mention above that this work focused on the effect of pH on the hollow sphere of $Cu_2O$. We first synthesized at pH 7 and found that $Cu_2O$ was yielded easily at low temperature. The reaction can be succeeded in only 30 minutes. Then, the range of pH supporting the synthesis was conducted to verify the repeatability of the production under a variety of the pH conditions. The results were shown in Figure 2, elucidating that the hollow sphere of $Cu_2O$ could be synthesized under a diversity of pH scale from 5-10.

Herein, we proposed the self-assembly mechanism of copper (I) oxide hollow based on some information from the previous studies (Yokoyama et al., 2007; Lou, Archer & Yang, 2008). It was known that PONPE formed aggregation core as a sphere micelle with the outer active site of ethylene oxide (EO) unit encountered in the moiety of water. In the vicinity of $Cu^{2+}$, oxygen atoms of EO chains were the sites for $Cu^{2+}$ coordinating and forming crown-ether via oxygen lone pairs of each EO unit. Based on the numerous evidential research studies (Palmaa et al., 1998; Yoshihara, Tadokoro & Murarhashi, 1964), it is evidentially proved the interaction between PONPEs and polyvalent metal ion existing as crown-ether configuration. The studies were reported not only for oxygen linkage (Hammouda, Ho & Kline, 2002; Begum & Matsuura, 1997; Angelova, Manolova & Rashkov, 1995) but also for the phenyl linkage (Petrie, 2003). Then, the crown ether-like with copper ions was drawn in Figure 6.

To perform the interaction between $Cu^{2+}$ and PONPE, a set of the investigations using UV spectroscopy of pure PONPE with and without $Cu^{2+}$ was scanned and the spectrums were shown in Figure 6. The adsorption of PONPE after adding $Cu^{2+}$ (spectrum (c)) clearly showed the existence of interaction between PONPE-9 and copper ions after compared with pure PONPE-9 (spectrum (a)) and $Cu^{2+}$ (spectrum (b)). It is reasonable to believe that $Cu^{2+}$ was linked by EO 5-6 unit of a PONPE which short as

$[(Cu(EO)_6]^{2+}$ for the coordination of 6 existing in octahedral configuration. Because PONPE existed in water as the spherical micellar aggregation, a number of $Cu^{2+}$ existed as the precursors along the circumference of PONPE micelle surface (Self & Zhou, 2016).

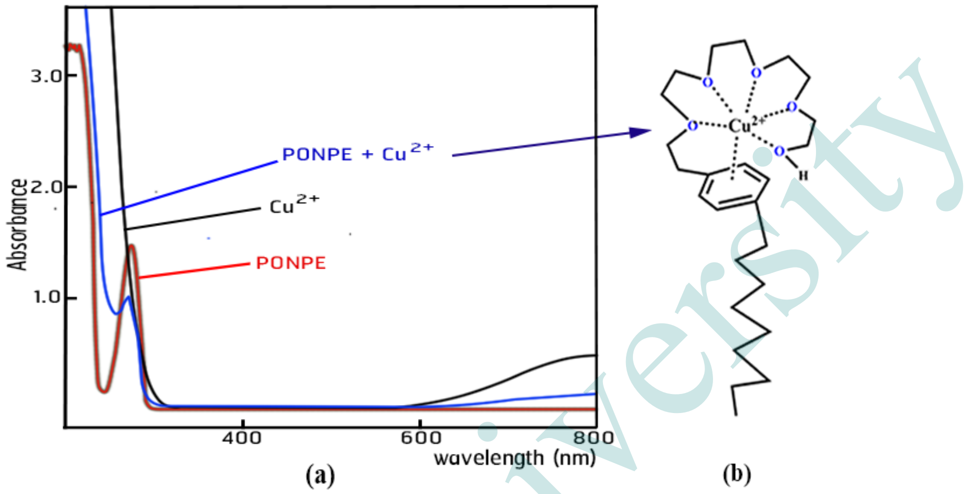

**Figure 6** (a) UV-spectrums of PONPE, $CuSO_4$, and PONPE-9 with $CuSO_4$ (b) the possible conformation of crown ether coordinated between PONPE and $Cu^{2+}$.

Based on the basic chemistry of $Cu_2O$ formation, the concentration of $[OH^-]$ must be high enough to displace EO ligands and form dihydroxo copper (II) ion before being reduced. The concentration of $OH^-$ at pH 3-4 was explained to be too low to substitute EO ligands and the reduction proceeded without the influence of $OH^-$. In a solution pH $\geq$ 5, the production of $Cu_2O$ suggested the replacement of $OH^-$ on EO ligands. It was curious to know the smallest mole number $OH^-$ required in copper (II) complex. The calculation based on two assumptions was attempted. First, the mole $OH^-$ in the complex was 2 which was the same as $Cu(OH)_2$. Secondly, the solubility product $K_{sp}$ was 2.2 x$10^{-20}$ by neglecting temperature dependent upon the equilibrium constant.

The equilibrium of $[Cu^{2+}]$ and $[OH^-]$ can be written as:

$$Cu(OH)_2\,(s) \rightleftharpoons Cu^{2+}\,(aq) + 2OH^-\,(aq) \qquad (5.6)$$
$$Ksp = 2.2 \times 10^{-20} = [Cu^{2+}]\,[OH^-]^2$$

The $[OH^-]$ required for the formation of $Cu(OH)_2$ in our synthesis was calculated. The experimental concentration of $Cu^{2+}$ (0.045 M) including Ksp of $Cu(OH)_2$ was subjected to the equation. $[OH^-]_{calculated}$ is found 6.99 x $10^{-10}$ mole/L providing pH of 4.9 $\approx$ 5. It was delighted that calculated pH (pH 5) matched the experiment (pH 5) for obtaining $Cu_2O$. Then, it was proven that the number of hydroxyl coordination to $Cu^{2+}$ must be equal or higher than 2 before being reduced to form $Cu^+$ and then $Cu_2O$ crystal, simultaneously. The reaction can be written as shown below (Saikova et al., 2010):

$$Cu^{2+} + PONPE \rightarrow [Cu(EO)_6]^{2+} \text{ (Crown ether structure)} \qquad (5.7)$$
$$[Cu(EO)_6]^{2+} + 2\,OH^- \rightarrow [Cu(OH)_2(EO)_4] = Cu(OH)_2 \text{ stabilized with EO} \qquad (5.8)$$
$$Cu(OH)_2 + e^- \rightarrow \tfrac{1}{2}\,Cu_2O + H_2O \qquad (5.9)$$

Since the mechanism of $Cu_2O$ formation was proven to be the same coordination number of $OH^-$ even in the presence or absence of PONPE. Then, PONPE functions only as the effectively shaping controlling agent as the soft micelle core.

$Cu_2O$ was then formed as the nuclei at the peripheral sites and subsequently individually grew up via the reaction of $Cu^+$ and $OH^-$ in the solution. Once the nuclei have grown, they become tiny clusters attached to each other around the outer shell of the micelles (Wang & Khachaturyan, 1995). The oriented attachment of the numerous tiny clusters forming spherical walls can be seen clearly in SEM picture depicted in Figure 7.

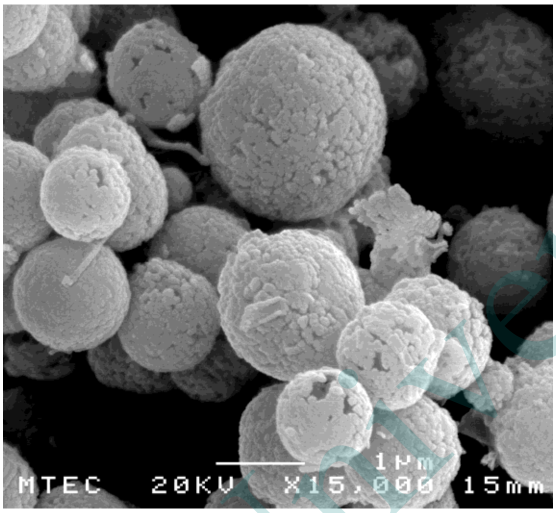

**Figure 7** The oriented attachment of the numerous tiny cluster of spherical hollow $Cu_2O$

Figure 7 showed the SEM picture of spherical hollow $Cu_2O$ showing the packing of the numerous tiny clusters along the surface of the crystals. Moreover, the other processes such as Ostwald ripening were also co-operative, resulting in the compact sphere surface (Yao et al., 2010; Zeng et al., 2007).

We also draw the schematic process describing the formation of spherical hollow crystal by the help of PONPE in Figure 8.

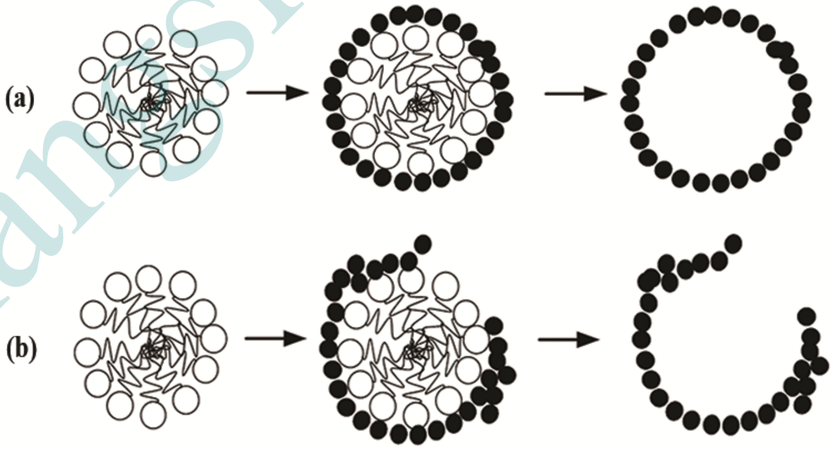

**Figure 8** The schematic illustration proposed for the self-assembly formation of hollow sphere $Cu_2O$ under the support of PONPE: (a) Perfect hollow sphere (b) Imperfect hollow sphere.

The graphical model of surfactant template before and after the coalescence of nanosized clusters of $Cu_2O$ over the sphere surface was shown in Figure 8 (Dang et al., 2011). We proposed a possible formation process of $Cu_2O$ hollow sphere for perfect and imperfect surfaces. In brief, the spherical micelle of PONPE was formed first, and $Cu_2O$ tiny clusters were grown and oriented attachment over the surface of the micelle sphere after the reducing agent was added. The surfactant disappeared in the washing process. The imperfect formation may result in the loose aggregates between tiny clusters as well as the disappearance of spherical surface which showed holes between clusters.

## 5. Conclusion

The synthesis using copper sulfate in the vicinity of PONPE-9 and ascorbic acid as the reducing agent was tested in a variety of pH range from 3–10. It was found that at the acidic pH from 3-4, the reduction in moiety of hydrogen ion yielded copper pure metal with the long geometrical rod-like shapes. The growth of geometrical rod-like shapes of pure Cu was explained with the preferable adsorption of PONPE-9 onto the specific facets of the crystals and allow the grown in one facet plane providing the long aspect ratio of the crystals. As for the synthesis at pH 5 up to 10, the increase of hydroxide ions supported the different reaction mechanism which yielded the hollow sphere of copper (I) oxide with the help of PONPE soft core. It was proved by the calculation under the equilibrium at pH 5 that $Cu_2O$ crystal was obtained after the formation of dihydroxo copper (II) ion which was corresponding to the mechanism of the synthesis in aqueous solution without a shaping agent. Moreover, this study supported the information on developing the industrial procedure for synthesis of $Cu_2O$ hollow sphere according to the easy handling of a wide range of pH of the reaction.

## 6. Acknowledgement

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