Int. J. Electrochem. Sci., 7 **(2012)** 4942 - 4950

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Synthesis and Characterization of Copper (I) Iodide Nanoparticles via Chemical Route

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Received: 2 March 2012 / *Accepted:* 21 May 2012 / *Published:* 1 June 2012

Polycrystalline of CuI nanoparticles were prepared via convenient liquid-phase route from the Cu^+-DMF solution precursor. A passivation layer of Cu^+-DMF absorbed on the particle surface were responsible for the nanoparticles formation. The broadening of XRD patterns showed that the size of CuI particle is reduced. The TEM image showed the spherical and well-dispersed of CuI nanoparticlest. The absorbance spectra were decreased with the addition of water. FTIR spectra confirmed the presence of C=O, C=N and C=H bonds. From the SEM and XRD results, we confirmed that the DMF played role as a stabilizing agent.

Keywords: Copper Iodide; nanoparticles; chemical route; passivation layer; stabilizing agent

1. INTRODUCTION

Recently, nanosize materials have been widely studied because of their better properties compared to the bulk size. They exhibit large specific surface area and size-dependent quantum confinement effects thus have distinct electronic, optical, magnetic, catalytic and thermal properties. They provide a unique opportunity to observe the evolving electronic structure of materials growing from molecules to bulk [1 – 4].

Cuprous iodide (CuI) has attracted much attention because of its unusual feathers such as large band gap, a negative spin-orbit splitting, an unusually large temperature dependency, anomalous diamagnetism behavior, large ionicity, new high pressure phase etc [5, 6] and potential applications in superionic conductor, solid-state solar cells, catalysis for synthesis of organic compounds and others [7].

Nanosize CuI is being pursued with great interest because of several possible technical applications in catalysis, drug delivery systems, separation techniques, photonics as well as piezoelectric and other dielectric devices [8]. CuI has been prepared by several different methods, such as iodination of Cu films, electrodeposition [9] pulse laser deposition technique [10] liquid phase reaction [11] and vacuum evaporation [12] γ-CuI nanocrystals have been synthesized by an ethanol thermal method [7], β-CuI were fabricated by a hybrid electrochemical/chemical method [13].

CuI can also synthesized by coprecipitation, sol-gel processing, microemulsion, hydrothermal methods, solvo-thermal methods, template syntheses, biomimetic syntheses [14] and others. Despite the exciting developments, finding the new route suitable for facile, scale-up synthesis and flexible experimental processing is still a current challenge to meet the demand of applications in the near future. In this study, we develop a chemical route to synthesis spherical CuI nanoparticles at room temperature.

CuI nanoparticles that are prepared by this strategy show good dispersion in the suspension. The possible mechanism of the formation of CuI nanoparticles is also discussed.

2. EXPERIMENTAL PROCEDURE

In a typical preparation procedure, 95 mg of CuI is dissolved in 5ml of acetonitrile under ultrasonic stirring. A transparent pale yellow solution is obtained. Then 10 ml of DMF is added into the solution and evaporated at room temperature. The solution now turns to the green colour. Subsequently, 10 ml of water is slowly dripped into the solution under mechanical stirring. The solution gradually faded and turned to cloudy.

This indicates the formation of ultrafine white particle. The particles are collected by centrifugal separation and purified by repeated centrifugation. The sample is characterized by X-ray diffraction Philips X'pert MRD diffractometer with CuK α radiation (λ = 1.5056 Å), Scanning electron microscope (SEM Philip XL40), Tranmission electron microscope (LEO Libra 120 kV), UV-vis absorption spectroscopy (CARY, 50 probe UV-vis) and Fourier transform infrared spectroscopy (FTIR spectrum Nicolet IS 10)

After the formation of CuI/DMF, the solution is dipped in a glass substrate and then placed in the oven for drying process for 1 hour at 100°C. The samples then tested for SEM and XRD.

3. RESULTS AND DISCUSSION

3.1. XRD analysis

Fig.1 shows the XRD patterns for bulk and nanoparticles of CuI.

The XRD patterns show that the peaks for bulk and nanoparticles CuI matched well with the standard fcc structure of CuI. The diffraction peaks corresponded to (111), (200), (220), (311), (400) and (331) planes of crystalline γ-CuI, respectively. No characteristic peaks of other phases are observed, suggesting that a pure γ-CuI compound exists. The diffraction peaks of CuI nanoparticles are obviously broadened and less intensified due to the size effect. The average particle size is calculated to be 8 nm by using Scherrer formula.

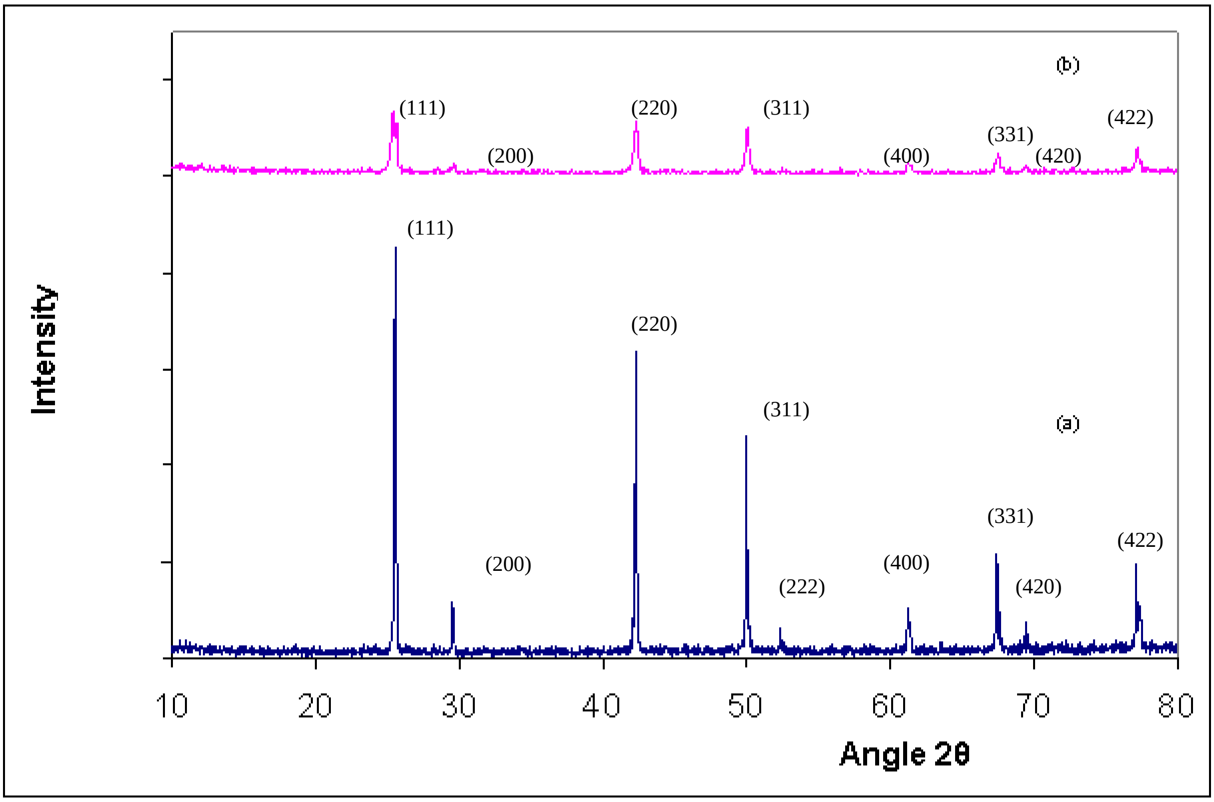

Figure 1. XRD patterns for (a) bulk and (b) nanoparticles of CuI.

3.2. SEM analysis

Figs. 2(a) and (b) show the SEM micrograph of CuI before and after synthesis

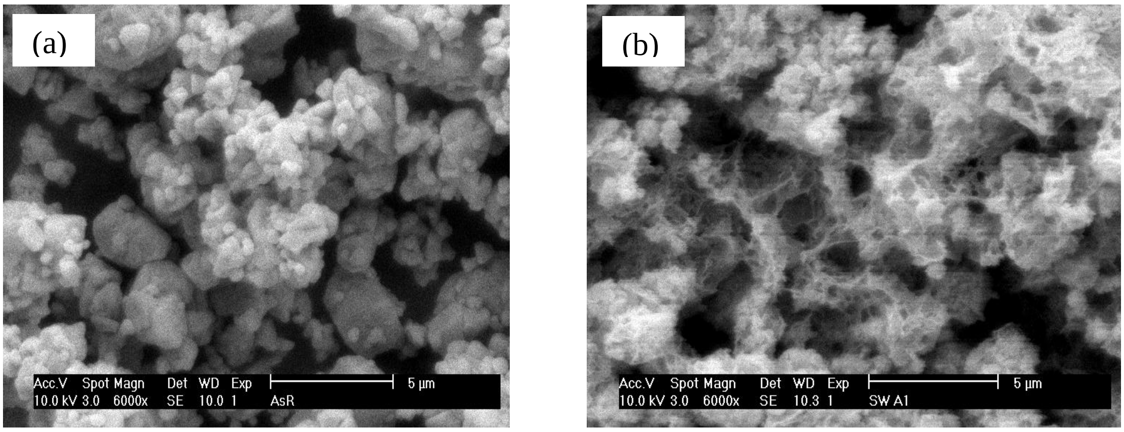

Figure 2. SEM images of (a) bulk CuI; (b) CuI after synthesis from precursor solution.

The SEM result shows that the CuI nanoparticles size greatly reduce after synthesis. However, the particles tend to agglomerate due to the formation of strong hydroxylic bond during drying. This will harden the particles surface and agglomerates the particles together which will lead to the formation of granules as shown in Fig. 2(b). Modifiers can be added to the aqueous solutions to prevent the coalescence of the nanoparticles. Nonetheless, this method will cause a negative effect which will results in formation of an impure product and it will then affects the application. The coalescence and agglomerations tendency of nanoparticles can be lowered if organic solvents are used instead of water. This is because organic solvents have weaker polarity compared to water and also no hydrogen bonds or Van de Waals forces will form. Alternatively, dehydrated organic solvents should be employed or reactions to be carried out under a protective dried nitrogen gas.

3.3. TEM analysis

Fig. 3 shows the TEM image of the CuI nanoparticles.

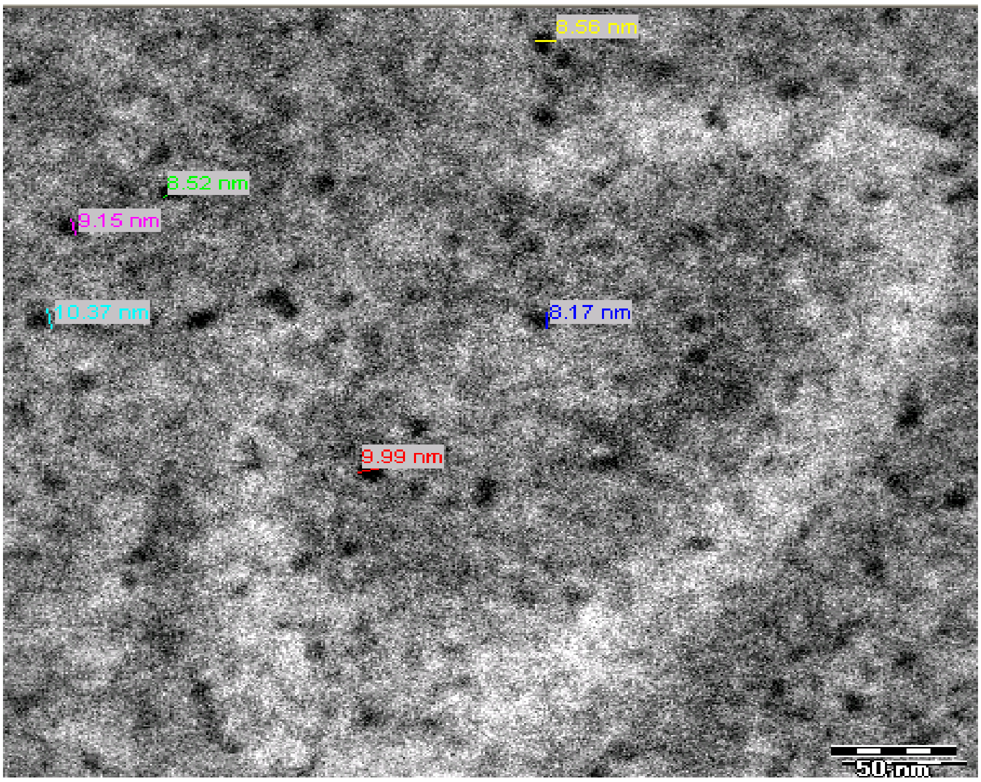

Figure 3. TEM image of the as-synthesized CuI nanoparticles

It can be seen that the nanoparticles formed are well-dispersed and evenly distributed in all direction. It is also very clear that most of the particles are spherical in shape. The average sizes of particles are in the range of 8 to 12 nm and calculated in good agreement with the crystallite size value from XRD.

3.4. UV – vis studies

Fig. 4 shows the absorbance spectra of CuI 10MF solution.

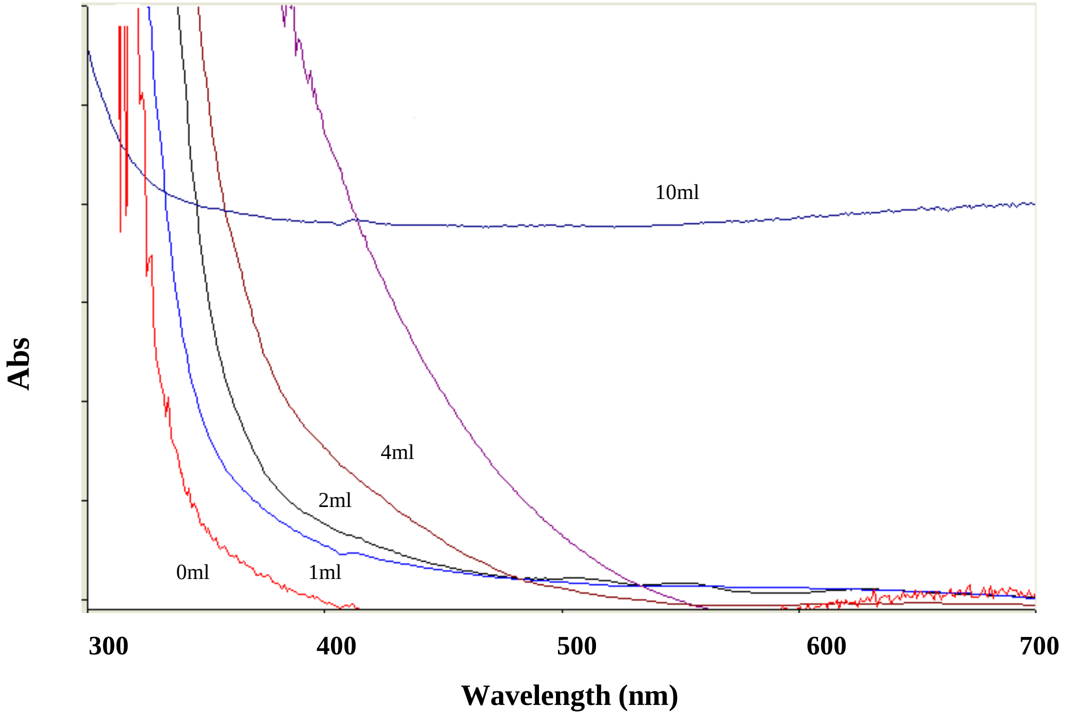

Figure 4. UV-VIS absorption spectra of 0.5mol of CuI in 10ml of DMF before and after water addition.

With the gradual addition of water the absorption intensity is quickly reduced. At the same time, an absorption peak at 406 nm grew and become saturated when 10ml of water was added. The peak position of 406 nm agrees well with the previously reported [15]. The absorption change demonstrates that water can decompose the complex in the solution and induce the formation of CuI, simultaneously.

3.5 FTIR Analysis

Fig. 5 shows the FTIR spectrum for CuI nanoparticles. It can be found that the peaks attributed to C=O, C-N and C-H stretching vibrations from DMF locate at 1659, 1415 and 1044 cm^{-1}, respectively. Due to the contribution of the two possible resonance structures of an amide, the bond order of the carbonyl C=O bond is reduced, while that of the carbon-nitrogen bond is increased. The spectrum shows a broad band between 3100 and 3600 cm^{-1} due to the intermolecular hydrogen bonding present in the water molecules. The stretching frequency of $3344cm^{-}1$ contributes to the O-H bond. This shows that the alkyl group is present in the system, due to the presence of ethanol or water.

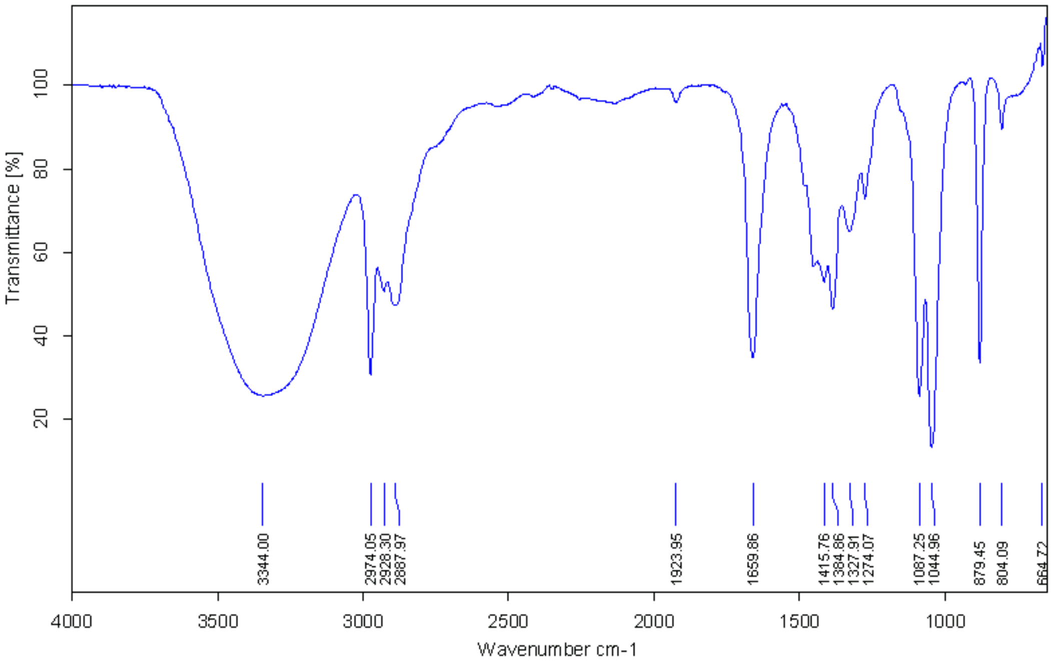

Figure 5. FTIR spectrum of CuI nanoparticles.

- *Formation of Cu-DMF Passivation Layer*

In this section, the role of DMF in CuI particle growth has been investigated.

- *SEM Analysis*

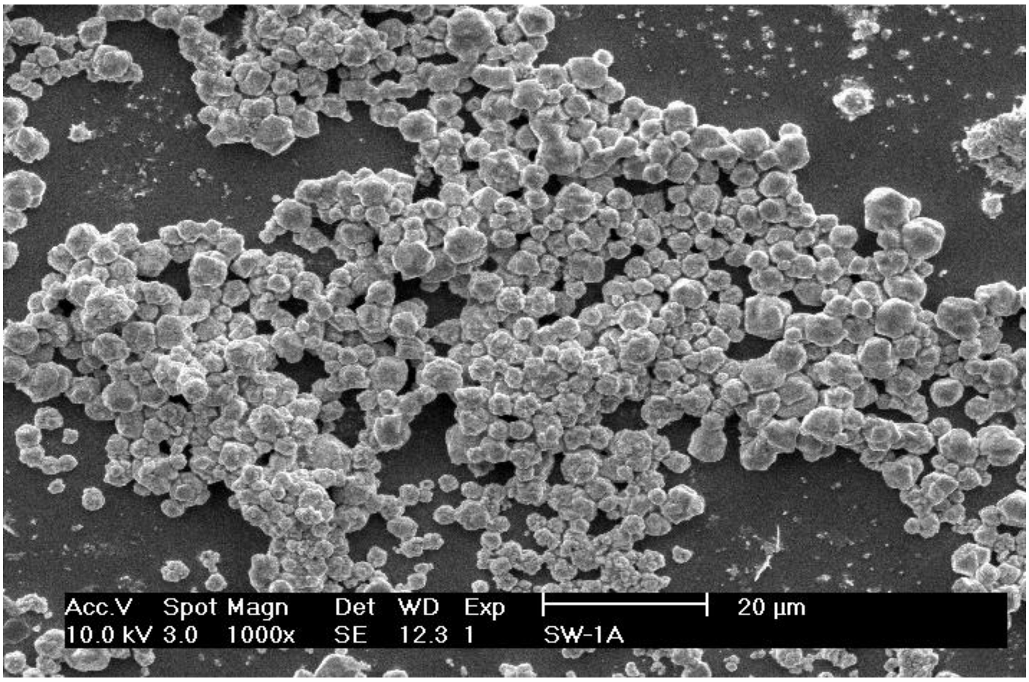

Figure 6. SEM image of CuI deposited on the glass substrate at 100°C

It is obviously seen that, the particle shape and size are more homogeneous after sintering. The particles are less agglomerated and the particle size increases to several microns due to the grain kinetic growth. The particle has the tendency to become single crystal, which is evident in the XRD result (Fig. 7). This will lead to thermodynamically stability and become more ideal. Thus, the role of DMF is very prudent as the stabilizing agent.

- *XRD Analysis*

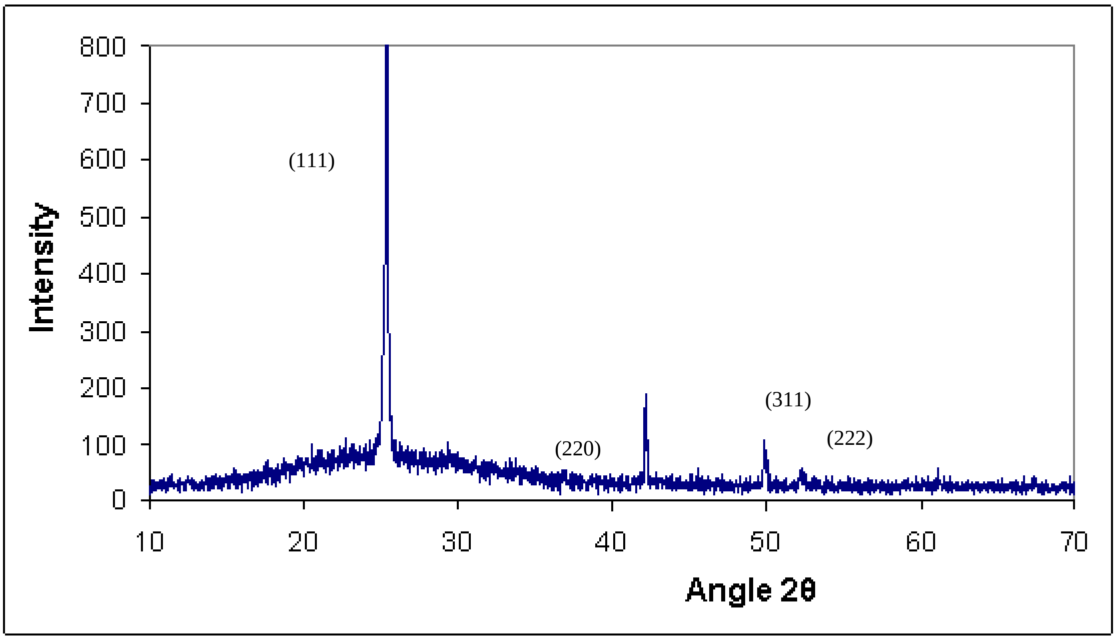

Figure 7. XRD pattern of CuI deposited on the glass substrate from CuI/DMF solution at 100°C

Fig. 7 shows the XRD pattern of the solid products on the glass substrate which four significant peaks are assigned to (111), (220), (311) and (222) planes for cubic CuI. The CuI deposited show less peaks as compared to the bulk and CuI nanoparticles as shown in Fig. 1. However, the deposited CuI on the substrate is highly orientated compared to the CuI nanoparticles which shows a tendency to become single crystal. The full width at half maximum (FWHM) line width for (111) peak is less than 0.1° indicated that it is highly crystalline. The life time of Cu^+ in water is usually very short. However, its relative stability can be strongly influenced by the nature of anions or other ligands present. It is reasonable to suppose that the $[Cu(DMF)_4]^+$ complex is the preferential species in the system. Iodine ion (I^+) might act as counter anion of this complex. Therefore, the role of DMF appears to be a stabilizing agent for Cu^+ in this system. The complex is decomposed into smaller CuI particles after the addition of water to the CuI/DMF solution. Nevertheless, DMF is still capable of reacting with the particle surface to form a layer of Cu^+-DMF capping each other as shown in Fig. 8 The observed colloidal stability is possible attributed to this surface passivation.

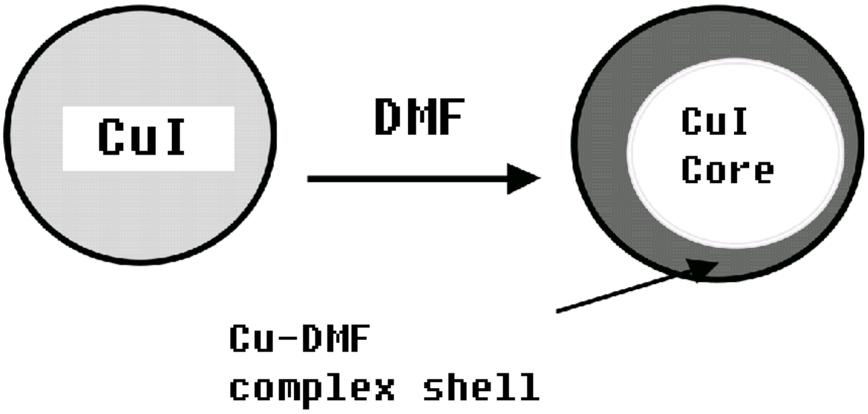

Figure 8. The capping of copper (I) iodide nanoparticles (CuI) with a Cu−DMF complex as a consequence of particle preparation in dimethyl formamide (DMF)

4. CONCLUSION

We have successfully prepared CuI nanoparticles via a simple liquid-phase route from Cu/DMF solution. Formation of nanoparticles was attributed to the Cu+-DMF passivation layer on the particle surface. The broadening of XRD pattern showed that the size of CuI nanoparticles reduced greatly after chemical synthesis. The calculated crystallite size is about 8 nm. The TEM results agreed with the obtained result from XRD. The size from the image is about 8 to 12 nm. TEM also showed that CuI nanoparticles are spherical in shape and are well-dispersed. SEM results showed that the CuI particles are evenly distributed but showed abit of agglomeration due to the formation of hydroxylic bond. From the UV-Vis analysis, it shows that the absorption intensity is quickly reduced with the gradual addition of water. FTIR analysis shows the presence of C=O, C=N and C=H bonds. The role of DMF in CuI particle growth is then studied which SEM image shows that the radius of nucleus grew due to kinetic growth and the particles tend to become single crystal after the addition of DMF. This showed that the DMF is a stabilizing agent. The XRD analysis showed less peaks and substrates are more highly orientated compared to as-prepared CuI nanoparticles. This again proven the role of DMF as stabilizing agent in CuI particle growth.

ACKNOWLEDGMENTS
The financial support received from Fundamental Research Grant, (FP 015/2008C) Ministry of Higher Education, Malaysia is gratefully acknowledged.

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