

Growth of nanosized cupric sulphate–urea complex in aqueous medium and its characterization

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Cupric sulphate-urea complex has been prepared in aqueous medium and growth morphologies of complex and reactants have been compared. Morphology of the complex is different as compared to those of the individual reactants. UV-vis spectra of pure cupric sulphate and aqueous solutions of complex prepared in different cupric sulphate and urea ratio show the maximum shift in λ_{max} when the molar ratio of cupric sulphate and urea is 1:2. Detailed investigation of the 1:2 complex has been carried out by IR, powder X-ray diffraction, thermogravimetry, differential thermal analysis and electron spin resonance studies. Surface topology of the complex has been studied by atomic force microscopy and the particle diameter observed by transmission electron microscopy. Nanosized complex is formed with particle diameter in the range 24-120 nm, while the average thickness of the particle is in the range of 634 -1260 nm.

Keywords: Crystal growth, Growth morphology, Nanomaterials, Cupric sulphate, Urea

Copper complexes have been studied extensively to model biological molecules that contain copper (II)¹. A number of copper complexes have shown promising anti-inflammatory activities.² Cu(II) ion can be embedded in the channels of urea to give complexes with thermal sensing properties³, Purakayastha and Baruah³ have studied the thermal sensing phenomena by resistance measurements. Metal-urea complexes may find applications in the fabrication of other more complex nitrides.⁴ Dissolution behavior of Cu(urea)^+ complexes generated by electrospray ionization has been studied by Schroder *et al.*⁵ They have studied electrospray ionization of aqueous solutions of Cu(II) salts in the presence of urea to generate the mono ligated copper(I) cation, Cu(urea)^+ . The gas phase reactions between Cu^+ and urea have been investigated by Luna *et al.*⁶ by mass spectrometry. The primary products

formed in the ion source correspond to $[\text{urea-Cu}]^+$, $[(\text{urea})_2\text{-Cu}]^+$ and $[\text{Cu}^+, \text{C}_2\text{N}_2\text{H}_2]$ complexes. The interaction of Cu^{2+} ion with DNA in aqueous solution containing urea was studied by Hackl *et al.*⁷ using IR spectroscopy. A urea complex of copper(II) hypophosphite was studied by Naumov *et al.*⁸ Cu(II)–urea complex has been synthesized and its thermal behavior studied by Radovanavic *et al.*⁹

Pattern formation has fascinated mankind for many years due to the development of the concept of fractal geometry in many fields including crystallization processes. A wide variety of patterns including concentric¹⁰⁻¹³, spiral,¹⁴ spherulitic and fractals¹⁵⁻¹⁹ has been observed in chemical and biological systems including the process of crystallization from their aqueous solutions. Herein, we report the experimental studies on the synthesis and characterization of nanosized cupric sulphate-urea complex by UV-vis, IR and ESR spectra, DTA, TG, XRD, AFM and TEM studies. The growth pattern of this complex has also been compared.

Experimental

Cupric sulphate (Glaxo, AR), agar-agar (Difco, Bacteriological grade) and urea (SD Fine, AR) were used.

Cupric sulphate-urea complex was crystallized from aqueous solutions of cupric sulphate and urea in 1:2 molar ratio containing ethanol. The solution was allowed to cool in ice for about half an hour. The blue coloured crystallized material was dried in vacuum.

Aqueous solutions of cupric sulphate (0.15 M), urea (0.15 M) and cupric sulphate-urea complex were prepared in 0.1% agar-agar medium. One ml of each solution was spread over microslides and allowed to crystallize in vacuum. Microphotographs were taken with an Olympus microscope fitted with the camera. Results are shown in Fig. 1 with the magnification given as bar diagram in the photograph.

UV-vis spectra of aqueous cupric sulphate and cupric sulphate containing urea in different molar ratios 1:1, 1:2, 1:3 and 1:4 were recorded up to 1000 nm on an Elico UV-vis spectrophotometer. Infrared spectra of urea and cupric sulphate-urea complex (1:2) were recorded on a Nicolet Impact 410 spectrophotometer. X-ray diffraction patterns of cupric sulphate, urea and

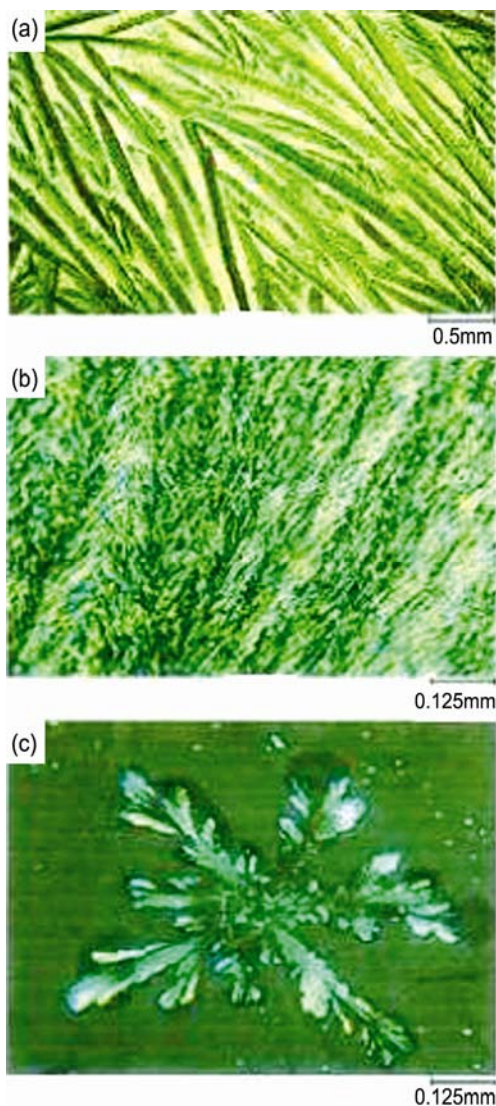


Fig. 1—Microphotographs of (a) cupric sulphate, (b) urea, and, (c) cupric sulphate-urea complex (in 1:2 molar ratio) crystallized from aqueous solutions containing 0.1 % agar-agar.

cupric sulphate-urea complex were taken using Rigaku RAD/MAX-B diffractometer (Rigaku Corporation, Japan).

Thermal characteristics of urea and cupric sulphate-urea complex (1:2) were investigated by TG up to 800 °C and by DTA up to 500 °C using Mettler Toledo differential scanning calorimeter (model DSC 821). Electron spin resonance spectra of cupric sulphate-urea complex (1:2) were recorded. Transmission electron microscopy of cupric sulphate-urea complex (1:2) was investigated using transmission electron microscopy (Philips, model CM 200).

The surface topography of urea and cupric sulphate-urea complex was investigated by atomic

force microscopy (NANO-R AFM System, Pacific Nanotechnology, USA), operating in close contact mode with substrate force constant of 40 N/m, resonance frequency of 300 kHz and tip radii < 10 nm. Lyophilized powder (~0.5 mg) of nanoparticles was dispersed by sonication in doubly distilled water (1 ml) to obtain a clear solution. About 2-3 μL of this solution was deposited in a “Piranha” cleaned glass slide and allowed to dry for 5 min at room temperature. Subsequently, the glass surface was imaged. Particle size was obtained using Nano Rule Software.

Results and discussion

Microphotographs of cupric sulphate, urea and the complex in agar-agar matrix are shown in Fig. 1. Morphologies of the reactants differ from those of the complex and the complex crystallizes in the form of fractal as shown in Fig. 1c. UV-vis spectra of cupric sulphate and cupric sulphate containing urea in different molar ratios show that maximum absorption was observed at $\lambda = 804 \text{ nm}$. On addition of urea in different molar ratios, a remarkable shift in λ_{max} value was observed in the case of the complex containing cupric sulphate and urea in 1:2 molar ratios. The IR spectrum of cupric sulphate-urea complex was interpreted with the assignment of the observed frequencies of urea as reference. For the free urea (symmetry C_{2v}), there are two types of NH_2 in-plane vibrations: (i) NH_2 bending motions in the region $\sim 1591 \text{ cm}^{-1}$ (A_1 mixed with carbonyl vibration) and antisymmetric (B_1), and, (ii) symmetric and antisymmetric in-plane rocking at $\sim 1155 \text{ cm}^{-1}$. The cupric sulphate-urea complex shows the presence of a carbonyl vibration at 1634.84 cm^{-1} as compared to urea at 1680 cm^{-1} . This indicates that a coordinate bond is formed between nitrogen and the metal atom and that oxygen is not a donor atom. The shift in this region is due to the formation of N-M bond ($\nu_{\text{M-N}}$ at 469.44 cm^{-1}) which (i) increases the electron demand by the donor nitrogen atom, and, (ii) blocks the resonance between this nitrogen atom and the carbonyl group. Both these factors bring about increased C=O double bond character. In addition to these bonds, the N-H stretching vibrations in free urea occur at $\sim 3260 \text{ cm}^{-1}$, while in the metal-urea complex due to coordinated NH_2 groups this bands occurs at a lower frequency at $\sim 3100 \text{ cm}^{-1}$. As a result of the formation of the N-M bond, the corresponding N-C bond acquires more single bond character, which shifts the $\nu_{\text{C-N}}$ absorption peaks to lower frequencies

($\sim 2361\text{ cm}^{-1}$) in metal-urea complex as compared to $\sim 2468\text{ cm}^{-1}$ in free urea. The five intense lines with corresponding I/I^0 values in the X-ray diffraction patterns of cupric sulphate, urea and the complex in 1:2 molar ratios are summarized in Table 1. Results show that the diffraction pattern of the complex is different from those of the reactants. The formation of a new product is also established by other studies. ESR spectrum of blue coloured complex shows the $g_{\perp}$ value as 2.00277, which is less than 2.5, indicating that the complex is paramagnetic.

Thermal characteristics of urea and the complex in 1:2 molar ratios were studied by TG and DTA

Table 1—X-ray diffraction patterns of cupric sulphate, urea and cupric sulphate-urea complex in 1:2 molar ratio

Cupric sulphate		Urea		Cupric sulphate-urea complex in 1:2 molar ratio	
2 θ	I/I^0	2 θ	I/I^0	2 θ	I/I^0
15.679	21	20.110	2	16.317	21
18.946	100	22.303	100	19.100	14
24.487	20	29.435	5	32.677	67
31.332	55	35.594	8	45.008	100
38.199	19	45.442	11	50.208	18

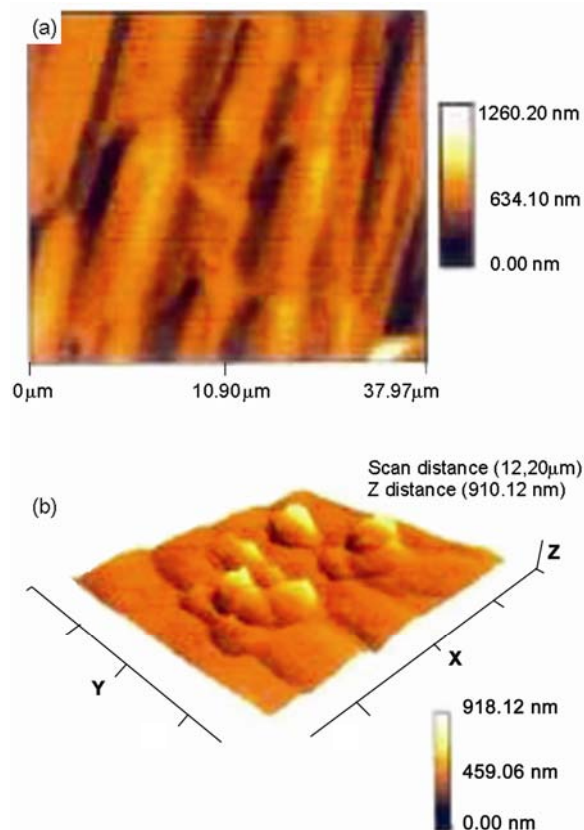


Fig. 2—AFM images of (a) urea and (b) cupric sulphate-urea complex in 1:2 molar ratio.

studies. Urea decomposes in three stages in the range (i) 135–240 °C with corresponding 59.1 % weight loss, (ii) 240–260 °C with corresponding weight loss of 26.70 %, and, (iii) 360–600 °C with more than 13 % weight loss. On complexation with Cu^{2+} ions, it decomposes in three stages in the range: (i) 75–140 °C with corresponding weight loss of 28.01 % due to dehydration, (ii) 210–270 °C with corresponding weight loss of 7.26 %, and, (iii) 470–700 °C with the corresponding weight loss of 39.42 %. Results indicate that the stability of the complex is more than that of urea. The results further show that the complex is unstable beyond 470 °C. DTA results of urea and the complex are different. Urea shows its melting point at 134.29 °C while the complex shows three endotherms at 107.5 °C, 126.68 °C and 252.21 °C. Together with the TG data, it may be inferred that the first endotherm corresponds to dehydration, the second endotherm due to melting of the complex and the third endotherm due to decomposition of the complex. The corresponding heat changes (ΔH) were determined by comparing their peak areas with that of benzoic acid for which heat of fusion is known (3.87 kcal/mol) using the expression $\Delta H.m = KA$, where m is the mass of sample, K the calibration

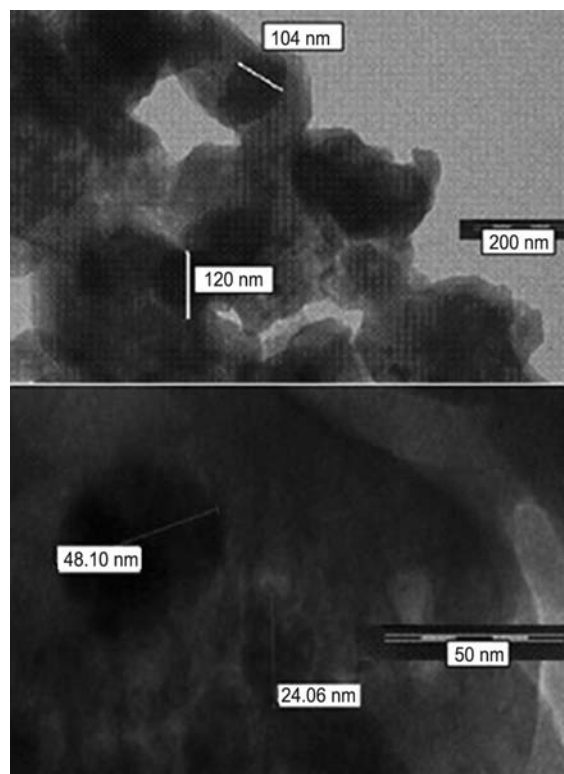


Fig. 3—TEM images of cupric sulphate-urea complex in 1:2 molar ratio.

coefficient and A is the peak area. The corresponding ΔH values were found to be 11.19, 8.96 and 10.08 kcal/mol respectively. The surface topography of urea and the complex in 1:2 molar ratios was studied by using AFM (Fig. 2). The average thickness of the particle aggregates was in the range of 450-918 nm, lower than that of the urea (Fig. 2a), as indicated by AFM studies. TEM studies revealed the formation of nanosized material with particle diameter in the range 24-120 nm as (Fig. 3).

In the present study cupric sulphate-urea complex was prepared and the reaction product of 1:2 molar ratio was characterized by various techniques, viz., growth morphologies, UV-vis and IR and ESR spectra, XRD, TG, DTA and AFM studies. TEM studies reveal the formation of a nanosized material. On addition of urea in different molar ratios (1:1, 1:2, 1:3 and 1:4) to the aqueous solution of cupric sulphate, there was a remarkable shift in $\lambda_{\max}$ values. Maximum shift in the $\lambda_{\max}$ was observed when the cupric sulphate and urea were taken in the 1:2 molar ratio. Morphology of the reaction product, XRD patterns, TG, DTA studies indicate the formation of a new material. TEM studies reveal the formation of nanosized complex with particle diameter in the range 24-120 nm.

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