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Effect of N-complexing agents on the supercapacitive properties of reflux deposited CuO thin films

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Abstract

Synthesis of crystalline CuO thin films with porous mesh like fabric base on to stainless steel substrate was employed by means of the distillation type simple reflux method at the optimized temperature 70^0C. The effect of nitrogen based complexing agent such as urea and ammonium persulphate (APS) on the structural, morphological, electrical and supercapacitive properties of the copper oxide (CuO) thin film has been studied. Urea and APS as complexing agent was found to reduce the deposition-rate, which is due to the higher complexation as well as slowing down of the generation of Cu^{2+} that helped to improve the morphology of CuO thin films. Mixed phase of CuO thin films having monoclinic structure was found from the X-ray diffraction study. Hydrophilic nature of the CuO thin films was revealed from the wettability test. The electrical resistivity measures the charge transportation mechanism. Maximum specific capacitance i.e., 548 F g^{-1} at a scan rate of $5mV.s^{-1}$ in KOH electrolyte was found for the CuO thin films synthesized with APS. The electrochemical impedance measurement (at open circuit voltage, in the frequency range 10^5 to 10^{-2} Hz) exhibit an ideal supercapacitor behaviour due to occurrence of a vertical line, while at higher frequency an appearance of semicircle indicated the interfacial charge transfer resistance. This interconnected property strongly signifies that the formation of the CuO thin film can act as supercapacitor electrode.

Keywords: Reflux method, Copper oxide, Thin film, Complexing agents.

Introduction

In recent years, electrochemical supercapacitor electrode have proved to be of potential use in order to provide increased demand of energy sources for industrial revolution and development of smooth life style. Maintaining that a series of the electrochemical supercapacitors in recent past have dented the image of the energy storage devices, which demonstrate the improving power density than battery as well as higher energy density than the conventional electrical double layer capacitors as a result of large surface to volume ratio, interconnected surface states of the electrode and exploitation of both faradic and non faradic process [1-4]. The micro-scale engineering of the supercapacitor electrode exploited novel materials such as carbon nano tubes (CNTs), graphene oxide, conducting polymer, metal oxides (MO) etc. [5-10]. Among these materials the MO has caught a great deal of attention of researchers, because of its current controlling nature gives a very well semiconducting behaviour. A good amount of literature is available on the MO thin film which exhibit the development of semiconducting thin film for the p-n junction based device formation such as diode, transistor, LED etc. [11]. In order to tune the supercapacitive properties of MOs, electrochemical engineering has been used by incorporating other elements in to the MOs such as various complexing agent. Most predominantly, MOs are well accepted materials for the proposed application due to their complex hierarchical nanostructure responsible for the current controlling mechanism.

On behalf, among the available MOs, copper oxide (CuO) is the most promising material owing to their advantageous physical as well as chemical behaviour and processing aptitude, including tuneable morphologies, controlling porosity, relatively inert surface electrochemistry [12,13]. Furthermore, desired elements are both cheap as well as plentiful in nature. Literature may includes some studies on these materials synthesized by advanced techniques [14,15] and also their structural, morphological and electrical properties [16,17], along with their semiconducting property, in the preparation of high T_c superconductor [18,19], gas sensing p-n heterojunctions [20], supercapacitors [21,22], but effect of complexing agent on the CuO thin film is rarely reported in the literature. This fact specifically motivates the study of CuO thin film that can eventually be used as potential parent material for the proposed electrochemical applications. It is cleared that electrical conduction process is depends on the composition as well as the structure of the synthesized sample. There are numerous methods which manipulate synthesis of copper oxide thin film. Their Structural, morphological and electrical properties are strongly controlled by the deposition conditions and methods [23,24]. Research on the MOs, therefore be focused on developing the various methods, which contributes the well disposed process and gives the simple eco-friendly route. Besides this, here we launch the distillation type reflux method for the synthesis CuO thin film. Reflux is reliable and well controlled method in the preparation of thin films with good homogeneity and crystallinity at low substrate temperature. It is distillation type technique involving condensation of vapours and returns of this condensate to the system from which it is originated. The actual photograph of the reflux method has been illustrated in the fig. 1.

In the present work, therefore specific attention is paid to synthesis of CuO thin film by reflux method. The approach used in this work was to investigate the basic properties viz. crystal structure, morphology, wettability, optical, and electrical parameters of the CuO thin films. It may manifest the growing interest in the CuO thin film with the application effect of various complexing agents viz. urea and ammonium persuphate. Mixed phase of CuO i.e. monoclinic and cubic is perceived at low temperatures while it is very difficult to occurrence of single cubic phase due to the imposed epitaxial strain at the time of growing mechanism. Herein, distillation type reflux method is investigated to deposit the CuO thin film for the supercapacitor application by exhibiting the excellent electrochemical performance. In order to achieve the fast capacitive response, high volumetric capacitance and porous nature occurred in the CuO matrix is particularly important for the supercapacitive material due to electron/ion adsorption and unhindered mass transport during a reversible redox reaction process. Charging-discharging process also depends on the pores of different size [21]. The electrochemical properties are examined by means of the 5 M KOH electrolyte. CuO with ammonium persulphate electrode (CuA) exhibit maximum specific capacitance 548 f g^{-1} at 5 mV s^{-1} scan rate. Also CuA electrode realized much higher energy density 79.7 Wh.Kg^{-1} in the 5 M KOH electrolyte. Most interestingly, electrochemical impedance spectroscopy (EIS) measures the impedance in the linear regime, so that measurement remains consistent throughout [25]. Lastly our CuO system with different complexing agent can give a novel supercapacitor electrode due to dispersion and self-assembly occurs in the CuO electrode with the complexing agents provides a versatile approach to create unique nanostructures compounds for the proposed application.

Methods

The reflux method was used to synthesize the CuO thin films. For such a deposition, 0.1 M $CuSO_4$ solution was prepared in 100 ml beaker. Then in order to study the effect of complexing agent, 0.1 M urea and 0.1 M ammonium persulphate (APS) was added in two different beakers containing the above mentioned solution. Further these prepared solutions i.e. $CuSO_4$ with urea and $CuSO_4$ with APS were transferred into the flask of the reflux chamber where condensation process takes place. Cleaned substrates were vertically mounted in this chamber. The cylindrical flasks were heated up to 70^0C and kept for optimized time of 120 min. for the deposition of CuO thin films. When the solution bath attains the temperature 70^0C, the formation of the precipitation starts to takes place in the solution. After 2 h, formation of powdery CuO thin films is observed on the substrate surface. There after the films (nearly blackish in colour) are removed from the flask, washed with double distilled water, dried at room temperature and used for further characterizations. Henceforth, the prepared CuO sample with urea will be called as CuOU and the one with APS will be reffered as CuOA for further convenient use of study.

The thickness of the obtained thin films was measured by weight difference method using a sensitive microbalance. XRD analysis is carried out using Bruker made D2 phaser desktop unit with copper target and wavelength of 1.54 Å. Surface morphology is studied with the help of scanning electron microscope (SEM) model JEOL–JSM 6360. The surface wettability of thin film is evaluated by means of water contact angle measurement using Rame–hart USA equipment with CCD camera. The electrical resistivity measurement is conducted using standard two probe method.

Results and Discussion

Synthesis of CuOU and CuOA thin films by using reflux method is obtained by formation of precipitation in the solution. The reaction involves heating copper at optimized temperature in the presence of oxygen. The reaction leads to the formation of black coating on the copper surface. The growth kinetics of a thin film deposition proceeds by formation of clusters or nucleation and then further by growth of particles, which involves nucleation sites on the immersed surfaces. The slow release of Cu^{2+} ions is achieved using a complexing agent (ligand) to the Cu salt to form some copper complex species, which upon dissociation results in the release of small concentration of Cu^{2+} ions. Also, the different complexing agents release the ammonia, which further provides OH^- ions for complexing with Cu^{2+} ions forming a hydroxide. The possible general reactions for CuO thin film formation is as given below:

$$Cu^{2+} + 2NH_4.H_2O \rightarrow Cu(OH)_2\downarrow + 2NH^{4+} \qquad 1$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \qquad 2$$

Figure 1: Actual photograph of the reflux method

Fig. 2 shows the photographs of CuO thin films deposited onto stainless steel substrates and schematic of formation of different morphology. CuOU thin films were found to be brownish in colour, while CuOA thin film were slightly blackish in colour. It was seen that the complexing agent plays a significant role. Here, CuOA thin films (40 nm) were found to have lower film thickness as compared to the CuOU thin films (80 nm). This might be correlated to the fact that slow release rate of Cu^{2+} free ions concentration, which can be further equally correlated and seen from the obtained morphology. In case of CuOU randomness of the rice shaped grains was seen, which was rather self assembled in case of CuOA (see the schematics shown in Fig. 2).

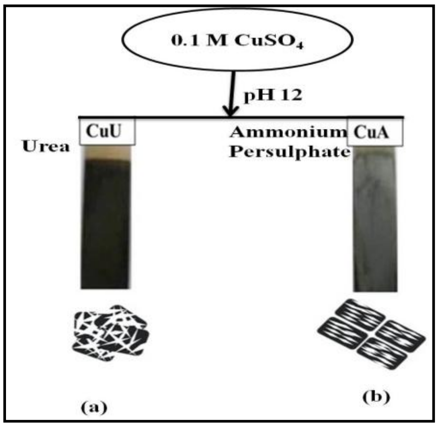

Figure 2: Schematic of chemical synthesis and photographs of CuO thin films on the stainless steel substrate.[Sample ID: CuOU and CuOA]

The X-ray diffraction (XRD) pattern of CuO thin film on to stainless steel substrate is shown in Fig. 3.

XRD peaks of CuOU and CuOA are consistent with the JCPDS file (JCPDS card no. 05-0661). The peak observed in both the CuO thin film samples corresponds to the crystalline nature of the sample, which are in good agreement with the recent observation [26,27]. CuOU sample exhibit high intensity peak corresponding to the plane ($\bar{1}$11) and (111); while in case of CuOA sample (020) plane was more preferred.

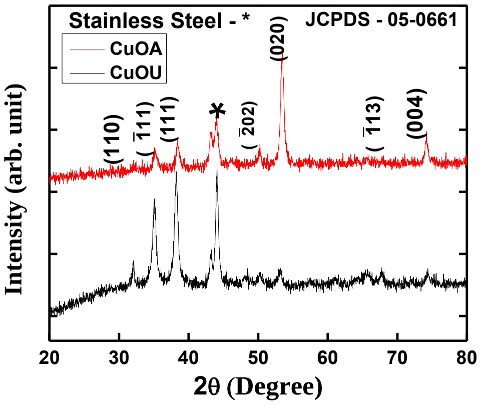

Figure 3: X-ray diffraction (XRD) patterns of CuO thin films deposited onto the stainless steel substrate [Sample ID: CuOU and CuOA].

From the XRD peaks, crystallite size is calculated by using the Scherrer formula [29] as given below,

$$D = k\lambda/(\beta \cos \theta) \qquad 3$$

Where, λ is the wavelength of radiation used, k is the Scherrer constant, β is the full width at half maximum (FWHM) intensity of diffraction peak for which the crystallite size is to be calculated, θ is the diffraction angle of the concerned diffraction peak and D is the crystallite size). Assuming k = 0.89, the crystallite size was calculated using the above formula for the most intense peak and is given in Table 1. It was seen that CuOU samples exhibited lower crystallite size as compared to CuOA samples. This suggests that the complexing agent i.e., urea and APS did have a substantial effect on crystal size. This fact is responsible for theto crystallites having more preferential orientation with high intensity towards the ($\bar{1}$11) and (111) in CuOU and (020) in CuOA samples. In fact the slower release of the Cu^{2+} ions by using APS as complexing agent helps in proper growth rate of the CuOA thin films [28].

Table 1: Crystallite size of CuO thin films samples (Sample ID: CuOU and CuOU).

Sample ID	Crystallite size (nm)	Resistivity (Ω.cm)	Activation Energy (eV)
CuOU	15.19	1×10^6	0.198
CuOA	20.08	2×10^6	0.673

The effect of urea and APS on the surface morphology of reflux synthesized CuO thin film was studied by using the scanning electron microscopy (SEM). Fig. 4 manifests the SEM micrographs of CuOU and CuOA sample obtained at ×15,000 magnifications. Randomly oriented fibre like mesh over which haphazardly distributed overgrown rice-shaped grains on a large area was seen for CuOU samples. However in case of CuOA samples, rather smooth porous fabrics of self-assembled square shape mesh on which uniformly distributed overgrown rice shaped grains was revealed. Such a well organized morphology in case of the CuOA sample may be due to the fact that urea is more basic than APS, which might lead to quicker reaction environment. A slow reaction growth in case of CuOA as compared to other one, might ultimately provides suitable time to well organize the structure, so that proper peripheral crystalline size may appear during the formation of thin film. The obtained porous structured films of CuOA may ideally be suited as energy storage electrode. The obtained results in SEM are in well consistent with the XRD data.

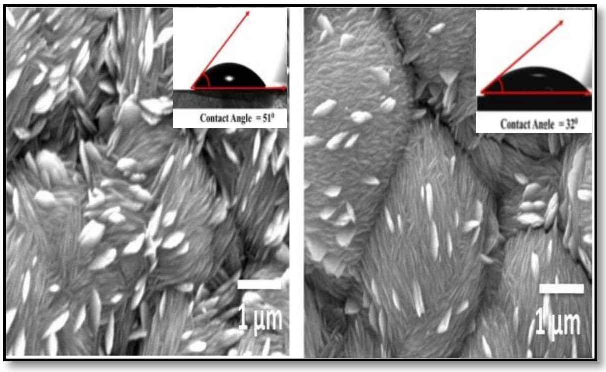

Figure 4: Scanning electron microscopy (SEM) images of CuO thin film at ×15,000 magnification [Sample ID CuOU and CuOA]. Inset shows water contact angle measurement of CuO thin films [Sample ID: CuOU and CuOA].

Furthermore, the surface porosity can be well studied through wettability properties of the sample. Wettability test measures the angle of contact between the liquid droplet and the surface of the thin film. As shown in the inset of Fig. 4, both the CuO thin film viz. CuOU and CuOA exhibit highly hydrophilic nature as a result of the sufficient oxidation. The contact angle of water on CuOA surface was seen to be 320 confirming the high wettability of CuOA sample surface. In contrast the CuOU sample shows the decreased hydrophilicity with a contact angle of 510. Thus increase in contact angle can be ascribed to removal of oxygen functional groups in CuOU films. This increased contact angle suggests that a higher reduction level in CuOA is achieved [30]. In addition to this the porous surface of CuOA can help to reduce the contact angle.

The electrical resistivity behaviour of the reflux synthesized CuOU and CuOA thin films with respect to temperature were studied by means of the two probe resistivity measurement set up. The obtained electrical resistivity data are shown in the Fig. 6. This resistivity can be measured by using the formula,

$$\rho = \rho_0 \exp(\frac{E_a}{kT}) \qquad 4$$

From the figure, it is seen that as the temperature increases resistivity goes on decreasing, indicating the semiconducting behaviour of both the samples. The resistivity of both the film is tabulated in the table 1. It is seen that resistivity of CuOA is one order higher as compared to the obtained resistivity of CuOU samples. Further, the activation energy of these samples was revealed from the equation:

$$E_a = 2.303 \times k \times slope \qquad 5$$

Where, Ea is the activation energy and k being the Boltzmann constant.

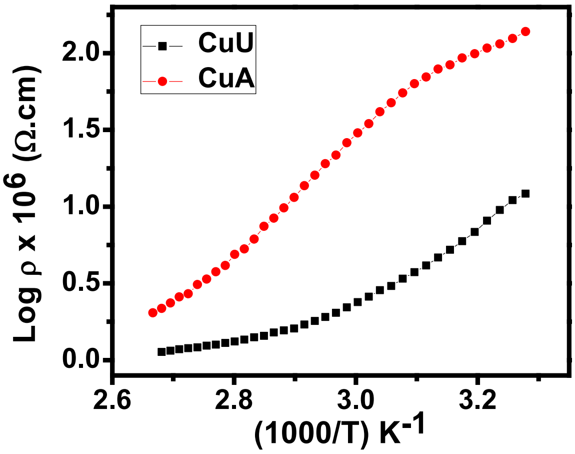

Figure 5: The variation of dc electrical resistivity (ρ) of CuO films in the temperature range 300–400 K [Sample ID: CuOU and CuOA]

In order to proceeds a chemical reaction at a reasonable rate, there exists the appreciable number of molecules with energy equal to or greater than the activation energy. The measurement of the activation energy corresponds to the overall leakage current during the electrochemical process [31]. The obtained activation energy is mentioned in the table 1.

The nanostructured CuO thin film electrode with mesh like porous fabric base displays an expert candidate for the electrochemical characteristic. Transportation of the electrolyte due to the faradic charge storage mechanism during the redox reaction attributes the supercapacitive behaviour. Difference in the orientation of the structure causes the difference in the charge storage mechanism. The electrochemical performance of the reflux synthesized CuOU and CuOA is investigated in three electrode system in by using 5 M KOH electrolyte.

The high or pulse power properties of the CuOU and CuOA electrode is examined by using the cyclic-voltammetry (CV) study. The CV curves of the CuOU and CuOA was obtained initially at different scan rate within the range -800 mV.S^{-1} to 200 mV.S^{-1} in 5 M KOH aqueous electrolyte to estimate the specific capacitance and the desired potential window was shown in the fig. 6. The voltammetric currents are directly proportional to the scan rate of the CV, indicating an ideal capacitive behaviour [32]. The specific capacitance of CuOA electrode is 548 $F.g^{-1}$ at scan rate 5 $mV.S^{-1}$ in 5 M KOH electrolyte; while in case of the CuOU electrode it is 229 $F.g^{-1}$. This might be because, the charge storage mechanism includes insertion/extraction of the cations into/from the first few nanometre of the electrode material. Therefore in case of the CuOA samples, the obtained square shape self assembled morphology with thickness 0.08 μm induces a very high capacitance due to high utilization of CuOA surface, which is in direct contact with the surface sheet and the electrolyte that result in to fast ion diffusion [33].

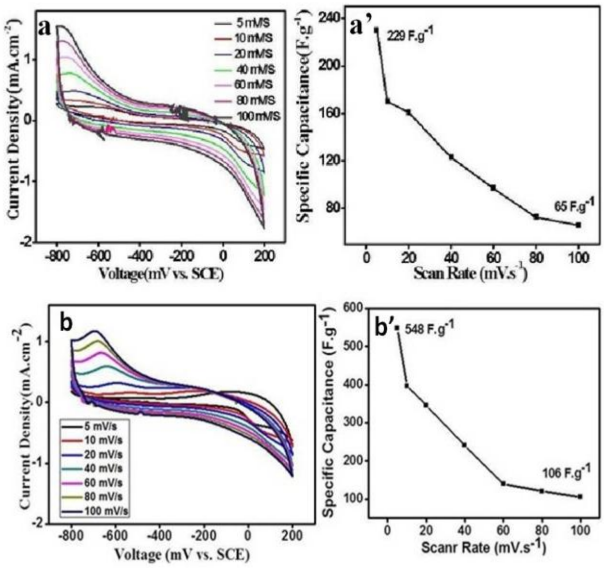

Figure 6: Scan rate variation and specific capacitance of CuOU and CuOA samples of CuO thin film electrodes in 5 M KOH electrolyte is shown in a, b and a', b' respectively.

Further, as the scan rate increases, specific capacitance goes on decreasing. This decrease in capacitance has been attributed to the presence of the inner active sites that cannot sustain the redox transition completely at high scan rate. This is probably due to the diffusion effect of the protons within the electrode. The decreasing trend of the capacitance suggests that part of the surface of the electrode is inaccessible at high charging-discharging rate [34]. The results obtained from fig. 6(a) and 6(b) are given in table 2.

Table 2: Specific capacitance at various scan rate of CuOU and CuOA thin film electrode in 5 KOH electrolyte

Sample ID Scan Rate($mV.s^{-1}$)	**CuOU** ($F.g^{-1}$)	**CuOA** ($F.g^{-1}$)
5	229	548
10	168	400
20	159	320
40	120	230
60	90	150
80	79	110
100	65	106

The galvanostatic charge discharge performance of the CuO electrode with the urea and APS as copmplexing agents was tested in 0.1$mA.cm^{-2}$ current density in 5 M KOH electrolyte shown in fig. 7.

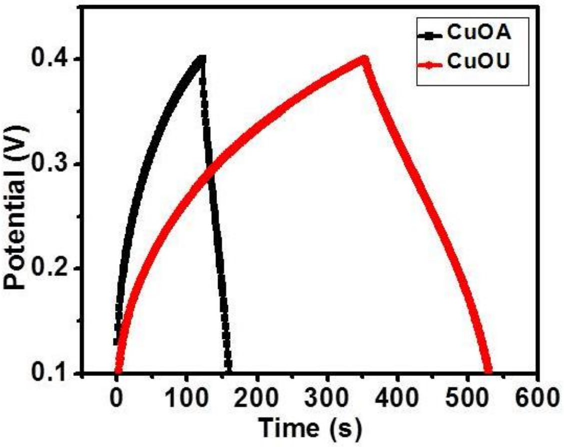

Figure 7: Charge-discharge curves different CuO thin films electrodes [Sample ID: CuOU and CuOA] in 5 M KOH electrolyte

Pseudocapacitive behaviour of the CuO samples is revealed from the charging-discharging mechanism. The discharging curve manifests three different part: Internal resistance of the material attributes to the initial drop in voltage, linear relationship between potential and time corresponds to double layer capacitance owing to the charge separation at the electrode-electrolyte interface and finally redox reaction between electrode-electrolyte understand by means of the slope variations [2]. Electrochemical parameters such as specific power (SP), specific energy (SE) were calculated using the following relations [35]

$$SP = [I\times V] / m \qquad 7$$

$$SE = [I\times t\times V] / m \qquad 8$$

Where, SP is specific power in $KW.Kg^{-1}$ and SE is specific energy in $Wh.Kg^{-1}$. The above expressions shows the discharge current (I) in amperes, voltage range (V) in volts, discharge time (t) in seconds and mass of the electroactive material (m) in kilograms. Specific power is depends on the utilization of the actual mass during the electrochemical process however specific energy is more precisely energy density quantify energy per unit mass. The CuOA electrode exhibit high SE up to 79.7 $Wh.Kg^{-1}$ and SP is 1.3 $KW.Kg^{-1}$. While CuOU electrode has SE 10.3$Wh.Kg^{-1}$ and SP is 0.71 $KW.Kg^{-1}$. The coulombic efficiency is calculated using the following equation [36],

$$\eta=[t_D/t_C]\times 100 \qquad 9$$

Where, t_C and t_D represent the charging and discharging, respectively.

This coulombic efficiency describes the efficiency with which charge (electron) transferred in a system facilitating an electrochemical reaction. Coulombic efficiency of both the sample has approximately same in value. In case of CuOA electrode it is 81% while in case of CuOU, it is 80%.

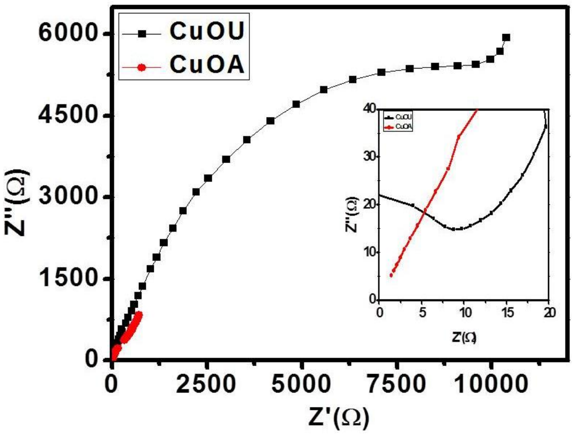

Figure 8: Nyquist plots of all CuO thin film electrodes [Sample ID: CuOU and CuOA] in 5 M KOH electrolyte.

In order to investigate the electrochemical characteristics of the electrode and electrolyte in quantitative manner, impedance measurements were performed. Nyquist plot of the CuOU and CuOA electrode in the frequency range 10^5 to 10^{-2} Hz was carried out in 5 M KOH electrolyte. As shown in the fig. 8, impedance spectra consist of semicircle at high frequency while at low frequency it has linear shape which shows the supercapacitive behaviour of the electrode material. Electronic and ionic resistances correspond to the equivalent series resistance (Rc) which can be evaluated from the intercept made on the X-axis [37]. The high frequency semicircle corresponds to the charge transfer resistance at the interface of the electrode and electrolyte solutions.

Conclusion

A distillation type simple reflux method was successfully launched for the synthesis of the CuO thin film with urea and the APS as complexing agents. Mesh like porous fabric nanocrystalline structure was deposited on to stainless steel substrate. Electrical measurement shows the semiconducting behaviour of both the CuOU and CuOA electrode. A high specific capacitance of 548 $F.g^{-1}$ is obtained at 5 $mV.S^{-1}$ for CuOA sample. Also the same electrode exhibit the maximum specific energy as 79.7 $Wh.Kg^{-1}$. The ideal supercapacitive behaviour of the CuOU and CuOA electrode can be revealed from the Nyquist plot at the electrode-electrolyte interface. From this data reflux synthesized CuOA electrode acts as a promising candidate for the supercapacitive electrode. The final summary is tabulated in the table 4.

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