Chapter 4

Highly Conducting Semiconductor Nanoparticles as Flexible Electrodes for Supercapacitors

4.1 Introduction

Nanomaterials cover a wide range of materials that includes metals, semiconductors and insulators [1]. In these materials various phenomena become a predominant with the reduction of size, as a result these exhibit interesting optoelectronic properties [2]. For example, in case of metals the reduction in size leads to the tuning of plasmon frequency that is collective oscillation of free electrons in response to the applied electromagnetic field [3]. Such materials are finding potential applications in large number of fields, including from plasmonic solar cells [4] to biomedical of selective tumour busting [5]. Where in case of semiconductor quantum dots the reduction of size leads to the controlled tuning of energy band gap and hence their optoelectronic properties can be turned over a wide range of energy [6]. Such materials are also expected to find wide applications.

Further, the semiconductors are broadly divided into two main categories: One is the conventional (or typical) semiconductors and other is the wide band gap semiconductors. As a result there are large class of materials that come under the semiconductor quantum dots, in certain cases the energy band gap has been tuned in the entire region of visible spectrum, these include CdSe [7], CdTe [8], CdSeTe [9], InP [10], CuInSe(S)₂ [11] etc. It has been anticipated that these materials find potential applications in almost all the branches of science and technology. It has been already shown that they can be put effectively for low cost solar cells [12], light
emitting diodes (LED) [13], photo detectors [14], chemical/biological sensors [15], quantum computing [16], for biological applications [17] etc.

In order to implement these materials for various applications, attempts are being made to dope the semiconductor quantum dots to achieve electrons/holes as a majority carriers and their density tunability [18]. These attempts are not so successful due to fact that invariably these materials feature a large density of surface states and also the bulk states, the latter is predominant if the crystallinity of particles is not good enough, these states leads to almost continuous distribution of energy states in the energy gap. This effect may pin the Fermi-level of these materials. However, in rare cases semiconductor quantum dots are made more conducting by making them either p-type or n-type without much control on carrier density tuning [19]. As a result their applicability for devices wherein a well defined interfaces are the essential requirements are limited [20]. Recently, certain type of semiconductor nanoparticles and their interfaces are implemented for energy storage devices, such as ion-insertion batteries and supercapacitor applications [21,22]. A brief summary of such materials is as follows. Composites of graphene oxide and needle like MnO$_2$ nanoparticles are implemented to design supercapacitors. The electrochemical properties of these electrodes are significantly enhanced by the chemical interaction these two phases [23]. Similarly, graphene nanosheets are interfaces with metal ions of Ni and Al to create the electrode materials. These composites exhibit the maximum specific capacitance 781.5 F/g with excellent life cycle [24]. Stand alone hierarchical structures of NiO are created in the range of nano to micro size to implement them for supercapacitor applications. These devices exhibited a good specific capacitance and retention with various electrolytes [25]. Exfoliated nanocomposites of MoS$_2$ are used as electrode materials for Li ion batteries and these devices are showing promising
performances [26]. Among many of these semiconductor quantum dots, the ruthenium oxide (RuO₂) and its composites with other functional materials are studied extensively [27]. Invariably all these semiconductor quantum dots feature the surface active sites that help to enhance the Faradaic reactions and hence the enhancement in the specific capacitance. There are many more semiconductor quantum dots that are implemented to ascertain their electrochemical performances [28, 29], still these materials and their applications to electrochemical properties are immature areas that need to be studied further before they see place for the market/commercial applications. In this chapter we discuss the highly conducting copper sulphide (Cu₂S) nanoparticles coated on the internal surface of cellulose paper to create high surface area, flexible, electrically conducting, simple synthesis and low cost electrode materials for supercapacitors. The procedure adopted here for the synthesis of these nanoparticles has been developed in our laboratory which is based on the complex formation between hydrazine hydrate and chalcogens [30]. Earlier, our group has prepared various high quality nanoparticles based on this route.

4.2 Present Investigations

4.2.1 Synthesis of Copper Sulphide Nanoparticles on Cellulose Paper

All the chemicals and reagents are used as they received without any further purification. For washing and reaction purpose triple distilled Milli-Q water is used. Copper chloride (CuCl₂), sulphur (S), hydrazine hydrate (N₂H₄), potassium chloride (KCl) and sodium hydroxide (NaOH) were procured from Himedia India. Tetraethylammonium tetrafluoroborate ((C₂H₅)₄NBF₄) (TEABF₄) and propylene carbonate (C₄H₆O₃) (PC) are obtained from Sigma-Aldrich, Germany. Copper sulphide nanoparticles were coated on cellulose paper by a simple chemical precipitation technique. In which 0.2 M CuCl₂ solution is prepared and then 2 cm x 2
cm cellulose papers were added to it. On the other hand, 0.1 M sulphur dissolved in hydrazine hydrate later in 95 ml of distilled water solution is prepared and added to the above mentioned CuCl$_2$ solution during the process of sonication uniform deposition of Cu$_2$S nanoparticles on cellulose is observed. Immediate precipitation takes place in the reaction; blue color solution of CuCl$_2$ turns to black after adding the orange sulphur solution. The cellulose papers also turn black in color confirming the coating of copper sulphide nanoparticles. Then these papers are removed from the beaker and washed with distilled water and sonicated to remove the loosely bound Cu$_2$S nanoparticles on filter paper. These were washed with plenty of distilled water and dried under table lamp. The sheet resistance of these sheets is observed to be around 80 $\Omega$/cm$^2$. This indicates that Cu$_2$S coated cellulose paper is highly conducting and is used for all the characterisation and also in the constitution of supercapacitors as described earlier.

The deposition mechanism of Cu$_2$S nanoparticles on cellulose paper is by chemical co-precipitation and is as follows. The modified chemical precipitation method is mainly based on the immersion of the cellulose paper into the cationic solution and sonicated thoroughly for the insertion of Cu$^+$ ions in to the pores of cellulose paper. Later the anionic precursor is added to the above mentioned solution and under the sonication anion and cation react and get precipitated as Cu$_2$S nanoparticles on cellulose surface covering both the outer and inner pores. This leads to high internal surface area. Figure 4.1 shows the schematic representation of Cu$_2$S deposition onto the cellulose paper. The cationic precursor for Cu$_2$S nanoparticles deposition is 0.2 M copper chloride (CuCl$_2$) solution complexed with 0.1 M sulphur dissolved in hydrazine hydrate acts as an anionic solution. By repeating such deposition cycles for 3 times, highly conducting and high porous cellulose papers
coated with strongly adherent Cu₂S nanoparticles are obtained.

![Figure 4.1: Schematic representation of copper sulphide nanoparticles on cellulose substrates.](image)

4.3 Results and Discussion

The mass of Cu₂S nanoparticles deposited into the cellulose paper is determined by gravimetric weight difference method by weighing the mass of the bare cellulose paper and Cu₂S deposited cellulose paper. For this a sensitive microbalance is used. The estimated amount of active material is 0.034g.

4.3.1 Structure and Surface Morphological Studies

Nanostructure of Cu₂S particles deposited on the cellulose paper is analysed using scanning electron microscope for their surface morphology. Bare cellulose images are shown in the Figure 4.2. Figure 4.2(a) is at the lower magnification and the same figure at the higher magnification is shown in Figure 4.2(b). Both the images are observed to be smooth without any coatings of the external material on the surface. Similarly SEM image of Cu₂S deposited cellulose paper with different magnifications are shown in Figure 4.3(a) and Figure 4.3(b). From this, it can be seen that the
Figure 4.2: Scanning electron microscope image of bare cellulose paper at (a) lower magnification and (b) at higher magnification.
**Figure 4.3:** Scanning electron microscope image of Cu$_2$S deposited cellulose paper at (a) lower magnification and (b) higher magnification.
cellulose paper is deposited with Cu$_2$S nanoparticles and the deposited nanoparticles are dense with visible pores on the surface. These recordings also show that the size of the nanoparticles is in the range 34 nm and 36 nm. Further it is noticed that the deposited nanoparticles are almost spherical in nature. In order to ascertain the chemical composition of these nanoparticles the energy dispersive X-ray analysis (EDAX) measurements are carried out. The results of these measurements are shown in Figure 4.4. The quantitative composition analysis of these papers shows that the copper and sulphur atomic percentage is 19.44 and 10.66 respectively, this confirms the formation of stoichiometric Cu$_2$S nanoparticle formation. Here important aspect is Cu$_2$S nanoparticles were deposited on cellulose paper, cellulose is the composition of carbon and oxygen atoms, hence in EDAX the more percentage of these materials are also observed, which is 36.02% and 32.84 % respectively.

Figure 4.5 shows the XRD pattern of a Cu$_2$S deposited cellulose paper. The formed compound is Cu$_2$S with hexagonal crystal structure. In the present case,
formation of Cu$_2$S is due to the addition of hydrazine hydrate, which acts as a reducing agent and releases Cu$^+$ ions instead of Cu$^{2+}$ ions from the CuCl$_2$ solution. The peaks of corresponding crystal planes were indexed in the figure, matching to the hexagonal phase of chalcocite β-Cu$_2$S (JCPDS No. 46-119, $a = 3.96$ Å, $c = 6.78$ Å). The broad peak near 23$^\circ$ is due to the substrate that is cellulose. The particle size of these semiconductor nanoparticles is calculated by using the Scherrer’s equation (equation 2.1, Chapter Two). The estimated particle size is about 37 nm. The present studies based electrical conductivity, XRD and surface morphology by SEM clearly confirm that small nanosize particles of Cu$_2$S semiconductor are coated on the cellulose sheet, covering both the external and internal surfaces, that are well connected physically. As a result, the resulting composite is highly conducting, flexible and having a large internal surface area. Hence, these electrodes can be a good material to build the electrochemical supercapacitors.

### 4.3.2 Electrochemical Performance

Further the Cu$_2$S deposited cellulose papers are used as electrodes to constitute supercapacitors with different electrolytes. The electrochemical properties are studied for these devices using Swagelok type cell or two electrode configuration (Figure 2.8, Chapter Two). The electrochemical properties are studied for various scan rates at ambient conditions, without sealing the supercapacitor under inert atmosphere. Figure 4.6(a) shows the cyclic voltammograms (CVs) of the Cu$_2$S deposited cellulose electrodes with 1 M KCl electrolyte with 2 V potential window, with different scan rates ranging from 2 mV/s to 120 mV/s. The CV curves on the negative voltage scan have the similar trace, indicating the reversibility of Cu$_2$S nanoparticles arrays on cellulose paper. The anodic current reaches highest value for the high scan rates at the applied potential of 1 V. This phenomenon is due to the redox reactions at the Cu$_2$S
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Figure 4.5: X-ray diffraction pattern of bare cellulose and Cu₂S deposited cellulose paper.

electrodes and the electrolytic ions. Within the potential range of -0.4 to 0.4 V, the small humps with corresponding anodic and cathodic peaks indicate that Cu₂S nanoparticles possesses pseudocapacitive properties, and the redox reactions may be involved in the transition of copper cations between Cu(0), Cu(I) and Cu(II) species [31, 32]. The oxidation of Cu₂S to Cu(III) species is unlikely to occur on the potential range of -0.6 to 0.5 V the phase transformation peaks are clearly observed in the mentioned potential limit denoting the pseudocapacitance property. Similarly supercapacitors were constructed using organic electrolyte (TEABF₄ dissolved in
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propylene carbonate). Figure 4.6(b) shows the CVs of the Cu₂S deposited cellulose supercapacitors constituted using organic electrolyte with 2 V potential window and along with different scan rates. In this particular organic electrolyte redox reactions are occurring between the surface of electrode and the electrolyte, hence the redox peaks are clearly seen in the CV curves in both anodic and cathodic regimes. This further confirms the pseudocapacitive behavior of the constituted supercapacitors using organic electrolyte with the Cu₂S electrodes. Also the representation of CV curves with various scan rates are shown in Figure 4.6(b). The current order for KCl is more as compared to the organic electrolyte. The measured current orders are 13.16 mA/cm² and 8.918 mA/cm² at 1 V for 120 mV/s scan rate for KCl and TEABF₄ electrolytes, respectively. It elaborates the ion transportation mechanism, in which ionic electrolytes leads the highest ion transportation hence the high current order while in case of organic electrolytes ion transportation is less leading to a small current. It may be due to the organic ion TEA⁺ molecule, which is bigger/heavier than the K⁺ ion that make ionic moment sluggish in the solution. This might be affecting the ion transportation and ion diffusion mechanism of constructed supercapacitors.

In both Figures 4.6(a) and 4.6(b) as the scan rate (S) increases, the anodic peaks shift towards the positive potential and cathodic peaks shift towards the negative potential, it explores the quasi-reversible nature of the redox reaction [33]. In cyclic voltammetry, the Randles-Sevcik equation describes the effect of scan rate on the peak current. The equations 2.14 and 2.15 (Chapter Two) and the linearity in \( i_p \) vs \( S^{1/2} \) provides the evidence for chemically reversible redox process versus the cases where redox causes major structural change in the analyte. The plots of cathodic peak current \( (i_p) \) as a function of \( S^{1/2} \) shown in the Figure 4.7(a) are nearly linear, implying that the electrochemical reaction is diffusion controlled in the electrolyte as
Figure 4.6: Cyclic voltammogram of constituted supercapacitors constructed using Cu$_2$S electrodes in (a) 1M KCl (b) 1 M TEABF$_4$ + Propylene Carbonate.
discussed in the *Chapter Two*.

In the same way the devices were constructed using 1M NaOH electrolyte, in this case the CV curves are appeared to be semi-rectangular curves for all the various scan rates as shown in the Figure 4.7(b). But for the high scan rate at higher potential a sharp peak is observed on both anodic and cathodic sides. In this electrolyte the non-faradaic reactions are responsible for the rectangular behavior, occurring between the electrode and electrolytic ions. Also cathodic and anodic currents are appeared to be same with negative and positive potential for all the scan rates.

From all the measured CV curves of constituted supercapacitors with different electrolytes, the specific capacitance values are determined by using the equation 2.10 (*Chapter Two*). All the evaluated specific capacitance values for three different electrolytes are plotted in Figure 4.8 as specific capacitance versus scan rates. From the graph it is clearly understood that the supercapacitor constituted using KCl electrolyte showed high performance with 3967 F/g at 2 mV/s scan rates. With increase in scan rate the specific capacitance decreased, it becomes about 1283 F/g for 10 mV/s scan rate. This shows ion transportation/diffusion is higher at the lower scan rate. Hence the high value of specific capacitance is achieved. Also organic electrolyte exhibited a specific capacitance of 1717 F/g at the scan rate 2 mV/s. Similarly for the NaOH electrolyte the observed specific capacitance is to be about 1052 F/g for the scan rate of 10 mV/s. Here for this particular electrolyte a small scan rate of 2 mV/s did not yield smooth CV curves and hence this scan rate readings are neglected. At present the exact reason for this is not clear, one possible reason for this could be the shorting of the two electrodes due to high ionic conductivity. However, the rapid fall in specific capacitance with increase in scan rate is routinely observed.
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Figure 4.7: (a) Randles Sevcik plot for 1M KCl electrolyte and 1M TEABF₄+PC (b) Cyclic voltammograms of constituted supercapacitors using Cu₂S electrodes with 1M NaOH electrolyte.
phenomenon in all almost the studies on electrochemical capacitors [34].

Finally, the cyclic stability tests were carried out for the above devices with different electrolytes. All the supercapacitors showed excellent stability with high specific capacitance retention for the smaller scan rates that is 10 mV/s measured for 1000 cycles, this data is shown in shown in Figure 4.9. It can be observed that the

![Graph showing specific capacitance values versus various scan rates in different electrolytes.

**Figure 4.8:** All the calculated specific capacitance values versus various scan rates in different electrolytes.
cyclic stability in all the devices is reasonably good as compared to the similar results on various supercapacitors constituted with different electrodes and different electrolytes [24, 25, 27]. It is noted that the KCl electrolyte supercapacitors showed 93.39% and NaOH 94.73% whereas organic electrolyte based supercapacitors showed the highest retention that is 97.47% among the remaining two electrolyte supercapacitors.

![Figure 4.9: Cyclic stability tests for all the three electrolytes](image)

**Figure 4.9:** Cyclic stability tests for all the three electrolytes
4.4 Conclusions

The Cu$_2$S deposited cellulose papers composite electrodes were successfully prepared in ambient conditions by a simple chemical precipitation technique. These electrodes are used to constitute supercapacitors with different electrolytes based on inorganic and organic electrolytes. Constituted supercapacitors exhibited an excellent specific capacitance of 3967 F/g for 1M KCl at the scan rate of 2 mV/s. Similarly the other two electrolytes also showed good specific capacitance at smaller scan rates. All the constituted supercapacitors are measured for cyclic stability at the scan rate of 10 mV/s for the three electrolytes with 1000 cyclic tests. All these electrolytes showed excellent retention. In case of KCl and NaOH electrolytes it is above 90% specific. It is interesting to note the retention is still higher in case of organic electrolyte that is close to 98%. Hence in conclusion, the new composite material based material highly conducting Cu$_2$S nanoparticles and cellulose paper are highly conducting, large internal surface area, flexible, simple synthesis and of low cost are the good materials for supercapacitor applications.
References


