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Review – Different Synthesis Methods of Copper Oxide for Supercapacitor Application

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***Abstract*: Copper oxide is a material that is of great importance for electrochemical performance because of its low cost and highly chemically stable nature. It is widely used for pseudocapacitive applications. The requirement for energy increases day by day. To fulfil the needs, we need to develop an energy storage device as well as an energy converter device. This review summarises the different synthesis methods of low-cost copper oxide thin film. The good result obtained by using a particular synthesis method was also discussed.**

***Keywords*: Copper oxide, Supercapacitor, Specific capacitance, Pseudo capacitor.**

1. Introduction

Copper oxide is a p-type semiconductor. It attracts researchers due to its remarkable electrical, magnetic, physical and optical properties [1], [2]. The band gap of CuO is 1.2 eV and is widely used in applications like catalysis [1], solar energy [3], field emission [4] and gas sensors [5]. Also, it is used in applications like photo-electro-chemical cells [6], batteries [7], the domain of energy harvesting and storage [8], photo-catalysts superconductors [9] and photovoltaic devices [10].

As copper oxide is non-toxic, it has enormous promise for biological and biomedical applications [11]. It has two types, one of such oxide is a cupric oxide (CuO), the other type is cuprous oxide [12], [13], and both types of copper oxides are semiconducting and offer interesting electrical and optical characteristics [14].

Supercapacitors are attracting wide attention due to its good reversibility, high power density and long cycle [15], [16].

According to the charge storage mechanism, supercapacitors are classified into two types: electrochemical double-layer capacitors (EDLC) and pseudo capacitors [17].

2. Methods of Synthesis of CuO

Various methods can synthesize the CuO. Various methods of synthesis of CuO also impact the specific capacitance of the material. Here, we will examine different synthesis methods for thin copper oxide films and nanoparticles.

Synthesis of CuO by sol-gel method: It is a very simple and fast technique compared to other synthesis methods, so it is widely used in designing nanomaterials [18]. This method was optimized to obtain the nanoparticles whose size ranged from 10 nm to 40 nm. So, it is often applied because of its control of nanoparticle size. Copper oxide nanoparticles were synthesized using the sol-gel method using *Lantana camara* extract as a mixture of $CuCl_2\ 2H_2O$ and NaOH. Lantana camera is a Verbenaceae family [19].

Dorner L et al. prepared the CuO using the sol-gel method. In preparing CuO, they follow the steps– preparing the starting solution by mixing the $Cu(CH_3COO)_2$ and $(NH_4)_2CO_3$. The following steps are nucleation, precipitation, washing, drying, and calcination. After that, we get the product as CuO. The steps are shown in the following figure [20].

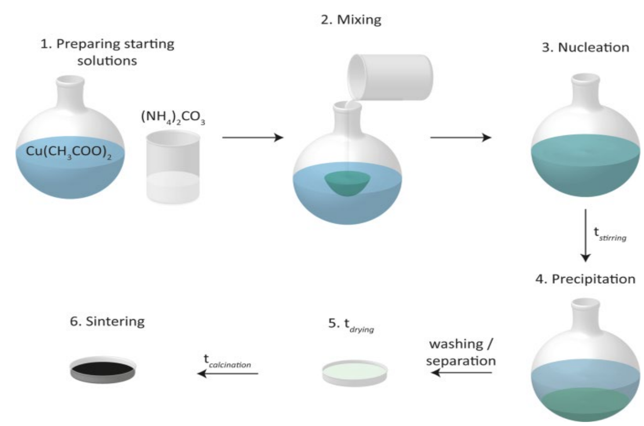

Fig. 1. Synthesis method of CuO by sol-gel method [10]

Monica Patel et al. also synthesized the CuO by using the sol-gel method [21]. In this method, the steps followed are taking 4.5 g of copper nitrate and 100 ml of ethanol and making the solution. Take a second beaker with sodium hydroxide and add 200 ml ethanol to it. Now, add this sodium hydroxide solution in the first solution dropwise, stirring constantly at normal temperature for 2 hours. Let the solution settle down, and then remove the upper layer. Now transfer the gel into centrifuge tubes and centrifuge at 10,000 rpm for 10 minutes. Remove the supernatant liquid and wash the sample with the distilled water. Repeat the step for 2-3 times. Dry the sample at 80^0 and then anneal it at 400^0 C for 2 hours in a muffle furnace. Finally, we crushed the annealed sample to get the CuO nanoparticles.

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Table 1

S.No.	Name of Material	Method of preparation	Specific Capacitance (F/g)	Reference No.
1	CuO	Sol-gel	180	23
2	CuO	Sol-gel	352	24

Table 2

S.No.	Name of Material	Method of preparation	Specific Capacitance (F/g)	Reference No.
1	CuO- N.P.s	Hydrothermal	197	27
2	$CuO@MnO_2$	Hydrothermal	184	28
3	MnO_2/CuO	Hydrothermal	167.2	29
4	CuO/Co_3O_4	Hydrothermal	666	30

Saja Mohsen Jabbar also prepared the CuO nanoparticles using this method [22]. The steps in the preparation of nanomaterials are – Saja Mohsen Jabbar took 0.9 g of copper (II) chloride, which was dissolved in 25 ml of ethanol, and this preparation solution of 1.5 g of sodium hydroxide was dissolved in 80 ml ethanol. This prepared sodium hydroxide solution was then added dropwise to the copper chloride solution with continuous stirring at room temperature for half an hour. Reaction occurs when the colour turns from dark blue to black. After the reaction filter paper is used to filter the gel and washed with water. The sample is then allowed to dry at room temperature and annealed at 700°C using a furnace. The annealed sample was ground. Hence, we obtained the fine nanoparticles of CuO. The table 2 shows the material *and its specific capacitance.*

Synthesis of CuO by hydrothermal method: The hydrothermal method of synthesis is a low-cost powder and thin film preparation method. This method can prepare a wide variety of thin films and powder samples. In this method, the parameters we can change are- temperature, time, pH of the solution, concentration of solution, etc.

Ahsan Habib et al. prepared the CuO nanoparticles by using hydrothermal synthesis [25]. The steps involved in the process are: First, add 0.2M $CuCl_2.2H_2O$ and 0.4M of sodium hydroxide in 40 ml of distilled water. The solution of aqueous NaOH was then mixed dropwise into the prepared solution under continuous stirring. Take this solution into a stainless steel autoclave, and it will be sealed and heated; wash the obtained black precipitate again & again. The final products were dried and filtered to obtain CuO nanomaterials.

The temperature of the autoclave changes at every reaction and the results were considered for three different autoclave temperatures. The temperatures are 105^0, 120^0 and 150^0 C. The U.V.- Vis absorption spectra study reveals that the CuO materials obtained at an autoclave temperature of 1050 C are good absorbers.

M. Ozga et al. prepared CuO by hydrothermal synthesis [25]. The paper uses this method to present the extremely fast growth of polycrystalline CuO thin films. The synthesis process takes place in an open system with a low temperature maintained (i.e. below 100 °C) and in a very short time (in the range of 6 min–38 s). It is not necessary to use toxic precursors for the growth of material. Also, there is no need for sophisticated equipment. For the synthesis process, the chemicals used are copper (II) acetate, sodium hydroxide (as a pH regulator) and deionized water. The synthesis method makes it possible to control the thickness of the thin films over a wide range. This paper discusses the impact of individual parameters, pH, heating power, process duration, and Cu(II) concentration on layer thickness.

Bharat R. Bade et al. synthesized the CuO thin film using this method [26]. The chemicals used for the synthesis are copper sulphate pentahydrate, ethanol, deionized water and NaOH as a stabilizing agent. In the experiment, first 0.5g CuSO4.5H2O was added into 100 ml deionized water under constant stirring for 10 min to get a clear solution. After 10 min constant magnetic stirring, 10 ml aqueous NaOH (2M) solution was added to the above aqueous solution under constant stirring to obtain a pH equal to 10 and a homogeneous mixture was formed. After completing the solution, the resultant solution was transferred into a locally made cylindrical autoclave having dimensions of 9cm × 1cm × 8cm (diameter × thickness × height) with 50 ml volumetric capacity Teflon leaned stainless steel autoclave. The reaction temperature was maintained at 180 °C for 20 hours. When the reaction was completed, the autoclave could cool naturally. When the autoclave reached a temperature equal to room temperature, the precipitate was taken out and centrifuged several times using deionized water and ethanol alternatively to remove the impurities from the solution. The centrifuged solution was kept in an oven and heated to 300 °C for 1 hour. Finally, we get the CuO thin films.

The table 2 shows the material and its specific capacitance.

Synthesis of CuO by Spray pyrolysis method: Spray pyrolysis is also a simple and low-cost synthesis method. If you have a setup installed, then using this setup, you can deposit various types of thin films, especially oxide materials. There are certain limitations to some types of material preparation using this method. However, for thin oxide films, it is a very good synthesis method. In this method, substrates are kept at a hot temperature, a temperature that can be kept constant by using a thermocouple. When the temperature is atomised, we spray the precursor solution at a fine flow rate, which is adjusted before starting the synthesis process. The schematic diagram is given in the figure 2.

CuO thin films were deposited very simply by Youcef Bellal et al. [32]. In preparing a thin film of CuO, the requirements are as follows: They used an empty spray bottle of perfume with a volume of 15 ml. It is filled with a desired precursor solution, a hot plate at high temperature (i.e. maintained at 550°C), ultrasonic apparatus, ordinary glass substrates and solvents for cleaning and preparation solutions. The precursor is copper nitrate and the solvents. From the XRD pattern, it is confirmed that the prepared sample is in the polycrystalline phase. It is a monoclinic crystal structure with orientation along (110), (002), (111), (200) and (020). The obtained band gap of material varies from 3.95 to 4.02eV.

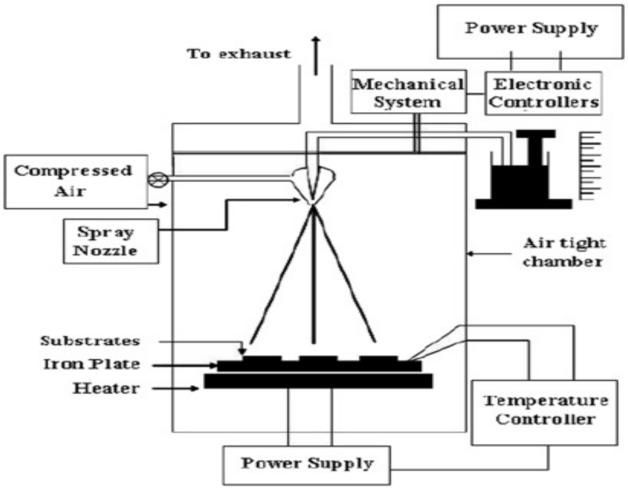

Fig. 2. The schematic diagram of the spray pyrolysis technique [31]

3. Synthesis of CuO by Chemical Bath Deposition

Chemical bath deposition (CBD) is another low-cost method for preparing CuO. The parameters in this method are temperature, time, pH, etc.

Nasser Saadaldin et al. prepared a thin film of copper oxide using chemical bath deposition [33]. In this method, the glass substrate is used. Copper oxide thin films were prepared by CBD methods by deposition of glass substrates using the Alternate Immersions method at room temperature for 20 seconds, which is very little time. Then, a heated liquid of sodium hydroxide was heated up to a temperature of 700, and the copper thiosulphate complex was used. The substrates were annealed at different temperatures (200-300-400) in the air. Finally, thin films of copper oxide are obtained. In this study, it is observed that the crystalline structure of prepared thin films was related to annealing temperature. Also, an optical study reveals that the band gap was also related to the annealing temperature. It varies from 1.3 to 2.4 eV.

Zainab M. Sadiq et al. prepared a CuO thin film using the single-step CBD method [34]. The CBD methods have various benefits, including that simple equipment such as a heating plate with a stirrer is sufficient for the entire process. There is no need for electrical conductivity in the substrate, i.e., you can also use the insulating substrate. Using this method, uniform thin films can be deposited [35]. Generally, the depositions are made at temperatures less than 100^0 C and may be applied to materials like polymers. Using this method, it is possible to cover complicated surfaces such as tubes, powder structures and porous structures [35].

4. Conclusion

CuO nanomaterials and thin films are low-cost materials with various properties and applications. The present study of CuO completely focuses on the various methods of synthesis of CuO. Also, it shows some remarkable results obtained in that research.

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