NanoScience Technology, Volume 4 (2022), pp: 1-16

NanoScience Technology

Journal homepage : https://jnanoscitec.com


# Application of copper oxide-based nanomaterials in electrochemical energy-storage devices

F. Rahimi[a], P. Eivaz khani[a], P. Kiyan Panah[a], S. Akbari[a]*

[a]*NanoSciTec GmbH, Hermann Weinhauser str. 67, Munich, 81867, Germany*

**Abstract**

Copper oxide is established as an important compound in technology due to its semi-conducting nature and high chemical stability as well as economic benefits. These features have made it a good candidate in energy storage applications. Further, extensive attention has been paid to advancement of supercapacitors- a complementary device between battery and conventional capacitors - due to their unique features such as high power, long cycle life, and environmentally friendly nature. In addition, copper oxide has sparked interest in preparation of applicable positive electrodes which can be used in preparation of supercapacitors. Meanwhile, copper oxide is mixed with polarized liquids and polymers easily, and it is has relative stable chemical and physical properties. Electrochemical features of copper oxide depend on the morphology where proper architectural design of electrode materials can be optimized in these devices. In this review, copper oxide synthesis and its redox mechanism as cathode materials will be explored as well as the application of various copper oxide compounds in preparation of high-performance supercapacitors.

Keywords: *Copper oxides, Supercapacitor, Electrode materials, Electrochemical energy-storage*

© Article info: Accepted by: 14 April 2022, Published by: 28 April 2022.

***Table of Contents***



* Corresponding author: S. Akbari. Tel.: +49-151-664-32106 E-mail address: somayeh.akbari@nanoscitec.com

## 1. Introduction

The application of electronic devices is inevitable in almost everywhere of modern human life from household appliances to medical instruments [1]. Electrochemical energy-storage (EES) devices, including batteries and supercapacitors, play an essential role in this area due to their energy conversion and storage abilities [2]. In addition, the adverse ecological impacts of fossil fuels and the intense desire to reduce the environmental pollutions have caused a revolutionary development in both sustainability and efficiency of EES [3]. Electrochemical capacitors, also well known as supercapacitors, are a group of electronic devices with ability to fill the gap between conventional plane-parallel capacitors and batteries due to their electrochemical properties [4]. Supercapacitors are divided into two categories including electric double layer capacitors (EDLCs) and pseudocapacitors based on the mechanism of energy storage and their active materials [5].

In EDLCs, the electricity is stored in the electrical field between separated plates where the charge storage takes place electrostatically (non-Faradaic) between electrode and electrolyte interface [6]. So, EDLCs can achieve fast charging/discharging rates and excellent cycling performance. On the other hand, the pseudocapacitors store charge through electrosorption, oxidation-reduction reactions, and intercalation mechanism [7]. They are ascribed to the fast and reversible redox process of active materials, such as transition metal oxides/sulfides and conducting polymers [8]. These kinds of materials exhibit relatively large capacitance values since the stored energy mainly results from a reversible redox reaction [9]. Transition- metal oxides such as $IrO_2$, $RuO_2$, $Fe_3O_4$, $MnO_2$, NiO, $V_2O_5$, and $Co_3O_4$ exhibit redox behavior and they have been used in pseudocapacitors along with a conducting polymers such as polyaniline (PANI), etc. [10].

Among various transition metal oxides, various types of copper oxide nanomaterials have attracted enormous attention in electrochemical energy-storage due to electronic, mechanical, and structural efficiency [11]. Furthermore, the beneficial properties of copper oxide such as low fabrication cost and high environmental stability as well as large pseudocapacitances have made it one of the best candidates in preparation of EES devices [12]. ]. Since the electrode type and electrolyte are two important factors affecting the supercapacitor properties, it is essential to apply a proper method for synthesis of CuO with a desired nanostructure. Various methods for synthesis of CuO nanostructures lead to preparation of different CuO nanostructures such as nanowires [13], nanoflowers [14], nanoribbons [15], nanohexagons [16], nanosheets [17], nanofilms [18], etc.

Some CuO properties such as its chelating effect in addition to surface catalytic effects have directed attention to CuO-based nanomaterials in comparison with other transition metal oxides. CuO is a p-type semiconductor with a narrow band gap, 1.2 eV, which is applicable to the design and construction of CuO hierarchical architectures for high-performance supercapacitors[19]. This review covers the recent developments in synthesis of nanoscale structures based on copper oxide especially the CuO in combination of other transition metal oxides, rare earth metals, as well as the organic compounds such as polymers. Various strategies have been developed for preparation of electrode where the influence of different factors is examined on energy density, power density, and cycle life.

## 2. Synthesis of CuO nanostructures

Nanoscale copper oxides have been studied extensively in the field of preparation of supercapacitors due to their tunable morphological properties, particle size, and composition as well as desirable size distributions. Diverse synthetic pathways including both chemical and physical strategies have been used in modulation of different parameters of CuO nanoparticles. There are some common strategies in CuO synthesis including solution-based methods, solid-state thermal conversion of precursors, electrochemical method, and thermal oxidation method. Solution-based synthetic method is flexible and suitable for large-scale nanoparticles production; among their various methods hydrothermal and chemical precipitation techniques have been widely used for CuO preparation [20]. Flexible adjustment of the metal ions source,

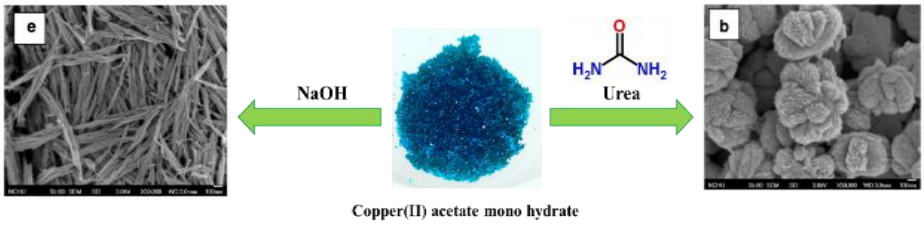


Figure 1. Effect of PVP on the morphology of the prepared nanoparticles.

applying water as a low-cost and environmentally benign solvent, and easy modulation of nanocrystal growth are some advantages of hydrothermal method. Generally, hydrothermal method is two-step process involving formation of the reaction of cupric salt precursor with a basic solution to form cupric hydroxide [$Cu(OH)_2$] particles followed by thermal dehydration of these particles in an autoclave at fixed temperatures to obtain CuO nanoparticles as final products. Chemical precipitation is another solution-based procedure for preparing CuO nanoparticles through chemical reaction between the precursors in an open container with a relatively low reaction temperature. The agglomeration of nanoparticles is one of the defects of precipitation method which can be improved by applying some external energy such as ultrasonic or high pressure in the separation step.

Solid-state thermal conversion or simply calcination of precursors is another method for CuO synthesis. This procedure is based on the synthesis of the Cu precursors by solving the cupric salt in an aqueous alkaline medium. The obtained cupric precursors are calcined in solid state after filtration and washing with distilled water plus absolute ethanol to obtain the final CuO nanostructures. The electrochemical method for preparing CuO nanoparticles is also very popular because of its advantages such as low-temperature, ease of process, and viability of commercial production. In addition, thermal oxidation is a simple, efficient, and low-cost method for synthesizing 1D CuO nanostructures, which is suitable for batch fabrication and mass production. Furthermore, the morphology, density, diameter, and length of the 1D CuO nanostructures can be easily tailored by adjusting the synthesis parameters. Sonochemical synthesis of CuO nanostructures has been reported by Anandan et al using copper acetate as a Cu source in alkaline media using urea/sodium hydroxide and in the presence of polyvinylpyrrolidone (PVP), as a stabilizing polymer [21]. CuO with quasi-spherical microarchitectures and long-straw like structure has been produced through the formation of a polymer–metal complex with the stabilizing polymer (PVP). In this procedure, the precipitate would be centrifuged and washed with distilled water and ethanol for several times. The resultant product would be dried under vacuum at 80 °C for about 6 h without any further thermal treatment or calcination. The stabilizing polymer (PVP) could be coordinated to metal ions before the reduction and this interaction may provide a different growth pathway leading to the formation of nanostructures of different morphology as displayed in Figure 1.

## 3. CuO nanostructures on Cu foams

The hierarchical structure of cathode is one of common electrodes in CuO-based supercapacitors which contain high mass loading of CuO with different morphologies. CuO is directly fabricated on the surface of copper-based foam or foil to form electrodes with excellent specific capacitance. Nanowires, nanosheets, and flower-like nanostructures of CuO formed on copper foam prepared by Cao et al. revealed a strong correlation between the specific capacitance of the nanostructured CuO and its morphology plus dimension [19]. The copper foam not only acted as a substrate of CuO formation but also was the current collector of the electrode. The anodization of copper foam followed by thermal treatments in KOH aqueous solution as electrolyte led to preparation of different morphologies of CuO arrays. Regarding the explanation of CuO formation mechanism on Cu foam by anodization, Cu was first electrooxidized to $Cu^{2+}$ and then combined with OH in the electrolyte solution to form $Cu(OH)_2$ precursor and finally converted to CuO during the subsequent thermal treatment. There

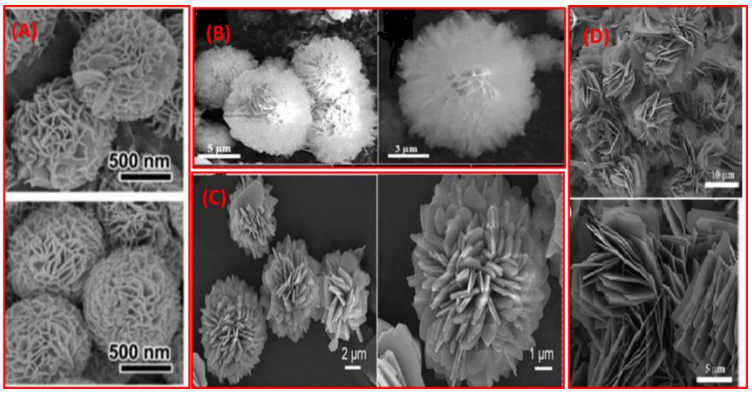


Figure 2. The relation between morphology of CuO and concentration of $(NH_4)_6Mo_7O_{24}.4H_2O$ (AM).

are two key factors in determining the morphology of CuO including the heating atmosphere and time. Nanowires were developed when the $Cu(OH)_2$/Cu precursor was heated in nitrogen for 3 hours and nanosheets formed when it was heated in air for only 15 minutes. The results indicated that the CuO nanosheets, composed of interconnected nanoparticles, with near vertical orientation on copper foam substrate, had a unique structure offering the CuO nanosheets' electrode a higher utilization efficiency and better property for electrolyte diffusion than the nanowires and the flower-like nanostructures. The nanosheet CuO exhibited the highest specific capacitance among the three different reported morphologies in this report.

Synthesis of copper oxide nanostructures using electrochemical anodization method offers numerous advantages including tunable and easy preparation, good repeatability, and good safety. Electrochemical anodization process has been used in the presence of $(NH_4)_6Mo_7O_{24}.4H_2O$ (AM) in the KOH electrolyte solution for preparation of single-phase CuO nanofilms grown directly on Cu foam [22]. The concentration of $(NH_4)_6Mo_7O_{24}.4H_2O$ directly affected the morphology of CuO nanofilms and accordingly formation of nanodots, nanoflakes, nanosheets, and/or nanobelts reported in this study. Figure 2 presents the relation between morphology of CuO and concentration of AM. Nanodot matrices studded with some flower-like nanoflakes formed in the absence of AM (Figure 2a). Addition of 5-10 $gL^{-1}$ AM to the electrolyte samples yielded very small nanoflakes and relatively long nanobelts (Figure 2b and c). In 20 g $L^{-1}$ AM, samples with a large number of nanosheet clusters were composed of some parallel nanosheets standing vertically on the substrate (Figure 2d). Samples prepared with an AM concentration of 40 g $L^{-1}$ are presented in Figure 2e where the Cu foam is compactly covered with NWAs with the morphologies of samples being nanobelts and nanosheets; elevating the AM concentration to 60 g $L^{-1}$ yielded very small clusters of nanosheets with a few radial nanowires interspersed among them. The results indicated that the as-fabricated single phase CuO nanosheet films exhibited a good areal capacitance greater than 600 mF $cm^{-2}$ at a current density of 1 mA $cm^{-2}$ in a KOH aqueous solution. Hydrothermal method was also used for synthesis of CuO nanofilm arrays on copper foam 1 M LiPF6/EC:DEC as electrolyte. The prepared CuO–Cu integrated electrode had unique nanostructure features such as large surface area and good electric conductivity, which led to high power density and energy density as well as high capacitances plus stable cycling performances [23].

The hierarchical nanostructure of lotus-like $CuO/Cu(OH)_2$ arrays directly fabricated on the surface of copper foil was synthesized by Hsu and co-workers via a simple and cost-effective liquid–solid reaction[24]. This electrode had an excellent specific capacitance of 278 $Fg^{-1}$, which corresponds to the energy density of 23.3 Wh $kg^{-1}$ by applying galvanostatic charge/discharge test at a current density of 2 mA $cm^{-2}$. In addition, the cyclability of the electrode demonstrates only a 15% loss in capacitance over 5000 cycles. Sonochemical methods were used to assist synthesis of various copper oxide morphologies

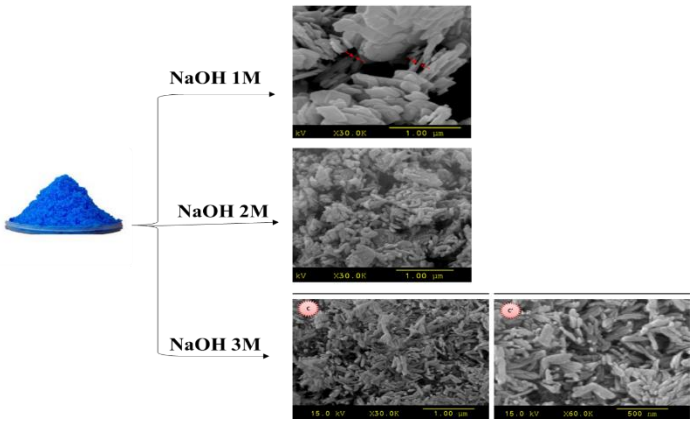


Figure 3. Illustration of the formation of $Cu_2(OH)_3NO_3$ nanoplatelets and various morphologies of CuO by controlling the reaction parameters.

without applying any templates or surfactants by Mousavi et al. [25]. The effect of different parameters such as high concentrations of $OH^-$, prolonging sonication irradiation, and thermal treatment on $Cu_2(OH)_3NO_3$ nanoplatelets as precursors led to formation of nanorods, nanoparticles, and nanospheres, respectively as shown in Figure 3. The different effects of different parameters such as high concentrations of $OH^-$, prolonging sonication irradiation, and thermal treatment on $Cu_2(OH)_3NO_3$ nanoplatelets as precursors led to formation of nanorods, nanoparticles, and nanospheres, respectively as shown in Figure 3. The specific capacitance of the prepared copper oxide nanostructures was evaluated by cyclic voltammetry (CV) at different potential scan rates in 1-M $Na_2SO_4$ solution as electrolyte. Accordingly, the prolonged sonicated sample (nanoparticles) showed a high specific capacitance of 158 $F.g^{-1}$. The results REVEALED that sample prepared in prolonged sonication (CuO nanoparticles) had the highest specific capacitance of 158 F $g^{-1}$ in 5 mV $s^{-1}$ in comparison with 110 and 92 F $g^{-1}$ for nanorods and nanospheres, respectively. Another report about developing synthesis of hierarchical copper oxide with a three-dimensional (3D) flower-like nanostructure has been presented by Zhao et.al. on a copper foam directly [26].

These novel synthesis strategies have some advantages such as providing massive active sites for redox reactions in the prepared CuO/copper foam electrode and high electronic conductivity, short diffusion pathway for ions, and effective electrolyte penetration. These characteristics together with the synergistic effect between CuO and copper foam substrate would lead to a high capacitance of 1641.4 mF $cm^{-2}$, good rate capability, and cyclability. Elsewhere, flower-like structured CuO nanoparticles were grown in situ on a 3D submicron-porous/solid copper current collector using $H_2O_2$ via a simple hydrothermal method [27]. This hybrid 3D network electrode had a high specific capacitance of 445 F $g^{-1}$ at 2 mA $cm^{-2}$ and 60.7% capacitance retention at a current density of 64 mA $cm^{-2}$ (270 F $g^{-1}$), high rate capability, and good cycling stability.

The application of template-assisted compounds such as CTAB can control the surface morphological features of the CuO nanostructure using co-precipitation method [28]. The concentration of CTAB affected the copper oxide nanoparticles morphologies. The cyclic voltammetric analyses confirmed the pseudocapacitor behavior of the CuO materials, providing a specific capacitance of 494 F $g^{-1}$ at a scan rate of 5 mV $s^{-1}$. The galvanostatic charge-discharge curve provided the maximum specific capacitance of 468 F $g^{-1}$ at a current density of 1 A $g^{-1}$. The cyclic stability showed that 94% of the initial capacitance was retained after 2000 cycles. CuO micro-balls and nano-hexagons were synthesized for super capacitor application in 6-M KOH solution specific capacitance of about 470 F $g^{-1}$ and 103 F $g^{-1}$ for CuO micro balls and nano hexagons, respectively [29].

The synthesis process is based on the concentration of OH- ions and temperature, initiating the nucleation and growth of primary 1D crystals. $NH_3 \cdot H_2O$ is coordinated to $Cu^{2+}$ at 4:1 ratio in basic media provided by $OH^-$. The intermediate $[Cu(NH_3)_4]^{2+}$ complex transports cations towards anion and OH- forms square planar complex of primary crystals of CuO nano rods. The following steps indicate the formation mechanism of CuO:

$$Cu + O_2 + H_2O + NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 4OH^- \quad (1)$$

$$[Cu(NH_3)_4]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 4NH_3 \quad (2)$$

$$Cu(OH)_2 + 2OH^- \rightarrow Cu(OH))_4^{2-} \quad (3)$$

$$Cu(OH))_4^{2-} \rightarrow CuO + 2OH^- + H_2O \quad (4)$$

**4. Successive ionic layer adsorption and reaction**

Successive ionic layer adsorption and reaction (SILAR) method is one of the best methods for depositing CuO in a thin film form based on successive immersion of substrate in cationic and anionic precursors with intermediate rinsing steps [30]. Copper sulfate and sodium hydroxide were used as cationic and anionic precursors, respectively. The SILAR system included four beakers applied for preparing different copper oxide nanostructures thin films. The cationic and ionic precursors were separated by two rinsing steps using double-distilled water. A clean stainless-steel substrate was immersed in a cationic precursor solution ($CuSO_4$) for 10 s for adsorption of copper species on it. Three different CuO nanostructures including nanoflakes, nanopetals, and diffused nanorods were synthesized through SILAR method simply by controlling the temperature of reaction bath. In this report, the anionic precursors were kept at three different temperatures for 10 s to form a layer of CuO material on the substrate. A total of 80 SILAR cycles were repeated to obtain terminal thickness of CuO thin films. Finally, the mass loading for samples at 45, 65, and 85 °C were found to be 0.61 mg $cm^{-2}$, 0.53 mg $cm^{-2}$, and 0.51 mg $cm^{-2}$, respectively. The SEM images of sample at 45 °C revealed uniform 3D flower-like CuO nanostructures with diameters of about 1–1.5μm. With increasing the reaction temperature to 65 °C, the surface morphology of CuO converted nanopetals clusters. When the reaction temperature was elevated to 85 °C, a remarkable change in morphology of CuO was observed where all nanopetals were dissolved in order to form diffused nanorods. The specific capacitances obtained for nanoflakes, nanopetals, and diffused nanorods at 5.6 A $g^{-1}$ current density were 623 F $g^{-1}$, 759 F $g^{-1}$, and 648 F $g^{-1}$, respectively. These good electrochemical properties were attributed to interconnected morphologies and providing large electrochemical active sites plus easy access for the electrolyte ions. Synthesis of binderless and surfactant free CuO films for pseudocapacitive applications by SILAR method was reported using indium tin oxide as substrate[31]. The morphology of the synthesized copper oxide had uniform surface and uniform pore distribution with average grain sizes of 30-50 nm. A specific capacitance of 566.33 $Fg^{-1}$ was obtained for as low as 10-cycle film at a scan rate of 5$mVs^{-1}$. The porous nanostructure of the electrode caused enhanced specific capacitance of CuO film. Elsewhere, SILAR method was also used for synthesis of $CuO/Cu(OH)_2$ hybrid thin film and well cleaned stainless steel as substrate[32]. Copper sulfate ($CuSO_4$) used as the cationic and sodium hydroxide (NaOH) as anionic precursors which kept at 300 K to form $CuO/Cu(OH)_2$ layer. The prepared nanostructures' diameters were 4–5 μm with a uniform flowerlike morphology. As each flower composed of many flake-like ultrathin nanopetals, they can generate abundant space facilitating the electrolyte ion transport. The interconnection between nanoflowers would provide a high volumetric specific surface area and good mass transport property causing highly reversible charge/ discharge features, with an excellent specific capacitance of 459 F $g^{-1}$. The cyclability of the electrode demonstrated only a 12% loss in capacitance over 2000 cycles. CuO thin films were synthesized on both steel and glass substrates by SILAR method with the average particle size of about 31.2 nm in order to enhance supercapacitor, photocatalytic, and ethanol sensing applications [33]. ]. The symmetrical shaped CV curves confirmed the suitability of the prepared electrodes for application. The maximum values of specific capacitance were 585 $Fg^{-1}$ and 554 $Fg^{-1}$ from the charging–discharging curve for the 30 cycles deposited film. It shows long-term stability with 92.3% capacitance retentivity after 4000 cycles.

## 5. Electrodes based on CuO in combination with other transition metals

The efficiency of the electrode materials can be enhanced by combining transition metal oxides with multiple electroactive redox sites. The electrolyte, separator, and the surface architectures of the material can also influence the supercapacitor efficiency. Transition-metal oxides are promising electrode materials due to their low cost, high chemical stability, and high theoretical Cs. The application of mixed metal oxides can improve pseudocapacitive performance as compared to employing the corresponding single-component oxides, so it is beneficial to obtain high electrical conductivities and Cs. The dopant can induce defection in the crystal structure by creating oxygen vacancies, which can enhance the net electrical conductivities and the final electrochemical performance. Furthermore, dopant ions itself can undergo electrochemical redox reactions, contributing to enhancing the net Faradaic involvement in the electrochemical supercapacitor. Further, the redox charge transfer usually improves when two metal oxide with different oxidation states are used together and represent a synergistic effect. Cu-doped manganese oxides have been investigated in preparing electrochemical supercapacitors. Komeily Nia et al. synthesized $CuO/MnO_2$ core/shell nanostructures and loaded them on nylon fabric for applications in wearable devices or smart textiles [34]. The divalent copper usually displays a poor distribution on synthetic fiber surface; so manganese was used to create complex with copper ions. The lower reduction potential of copper ions compared to the manganese ions led to synthesis of a core/shell structure with nanoflower morphology in which small coarse $MnO_2$ particles (shell) uniformly covered the preformed CuO (core). Improvement in the affinity of CuO nanoflowers toward the nylon fabric has synergistic effect of the synthetic method as well as self-cleaning and antibacterial properties on the fabric. In this report, Cu and Mn ions in the presence of $NH_3$ at a moderate temperature formed tetraamminecopper-(II)dipermanganate complex. Introducing a reducing agent such as NaOH first reduced the Cu ions due to the higher reduction potential than Mn ions with core/shell structure. Birnessite $MnO_2$-decorated hollow dandelionlike CuO architectures with $CuO/MnO_2$ core–shell structure were synthesized by Zhang et al. in the presence of tetraoctylammonium bromide as surfactant [35]. The prepared nanostructure had a good potential to be used as an efficient electrode for high-performance supercapacitors. The $CuO/MnO_2$ core–shell structures delivered high capacitance of 228 F $g^{-1}$ far beyond that of CuO dandelion-like structures, and a long-term cycling stability retaining 82.2 % of its initial capacitance even after 5000 cycles.

On the other hand, the preparation of $CuO@MnO_2$ core-shell nanostructures without any surfactants has been reported with energy density of 22.1 Wh $kg^{-1}$ and a maximum power density of 85.6 kW $kg^{-1}$ [36]. The $CuO@MnO_2$ core-shell nanostructure was used as the positive electrode and activated microwave exfoliated graphite oxide (MEGO) as the negative electrode to form an asymmetric supercapacitor with long-term cycling stability retaining 101.5% of its initial capacitance even after 10000 cycles. Recently, growth of $Cu(OH)_2$ nanofibers on the surface of carbon fiber in situ has been first reported by Wu et al. with a uniform distribution [37]. The further oxidation of $Cu(OH)_2$ converted it to CuO nanofibers and a layer of $MnO_2$ nanocoating grown in situ on the surface of CuO nanofibers to form the $CuO@MnO_2$ core−shell structure. The prepared electrode had a faster charge and discharge rate according to the results of the charge and discharge process with different current densities being shorter than that of other electrode materials. In addition, the CV curve profile remained essentially the same at different scanning speeds, yet it still retained 96.81% of the initial capacitance value after 5000 cycles of charge and discharge, showing a longer cycle life. A new hierarchical structure of copper oxide and manganese oxide hybrid has been fabricated using biominerals such as diatoms (unicellular algae) as natural templates in the form of $Diatom@CuO@MnO_2$ hybrid material [38]. Such a unique architecture acts as a supercapacitor electrode, which exhibits a high specific capacitance (240 F $g^{-1}$ at a current density of 0.5 A $g^{-1}$), good rate capability (58.3% retention when the current density rises from 0.5 to 5 A $g^{-1}$), and excellent electrochemical cycling stability (91.2% retention of the initial specific capacitance after 4000 cycles at a current density of 2 A $g^{-1}$).

$CuO–MnO_2$ composites have also been synthesized without any surfactant and in the presence of $Na_2SO_4$

electrolyte, leading to growth of the ultrathin $MnO_2$ nanosheets around nanopetals of flower-like CuO uniformly [39]. The results exhibited a specific capacitance of 167.2 F $g^{-1}$ and excellent cycling stability (88.6%retention after 5000 cycles). The flower-like CuO was self-assembled by some small nanopetals evenly decorated by some ultra-thin $MnO_2$ nanosheets after the hydrothermal reaction with $KMnO_4$. The uniform covering of CuO nano-needles by $MnO_2$ nano-sheets led to synthesis of $MnO_2$–CuO nanocomposites offering a good electrochemical behavior in a redox-mediated electrolyte of $K_3[Fe(CN)_6]$ in 2 M KOH [40]. Mn doped CuO thin films were prepared by Durai et al. using reactive radio frequency magnetron sputtering technique [41]. The galvanostatic charge–discharge measurements exhibited the areal capacitance of 87 mF $cm^{-2}$ at constant current density of 1 mA $cm^{-2}$ in KOH as electrolyte.

The synthesis of $CuFe_2O_4$/CuO nanocomposite has been reported by cathodic electrodeposition route as a facile, economical, and rapid process [42]. $Cu(NO_3)_2{\cdot}3H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ are to starting transition metal salts which fabricated a thin film of nanocomposite on the steel sheet surface by the galvanostatic mode deposition at the current density of 4 mA $cm^{-2}$. The final nanocomposite was prepared after the reaction completion and separation of black precipitate from the steel sheets followed by the calcination at 400 °C. The morphologies of $CuFe_2O_4$/CuO composite consisted of a highly porous dendrimer structure with the outer layer ending to microspheres composed of peanut-shaped or “necked” nanoparticles with their EDS spectrum being related to the characteristic peaks of oxygen, iron, and copper. The obtained nanostructures with specific capacitance of 322.49 F $g^{-1}$ at the scan rate of 1 mV $s^{-1}$ were a suitable candidate for application as practical materials for supercapacitor applications.

Cobalt-based materials such as cobalt oxides possess excellent capacitive performances so they have been investigated in high-performance supercapacitors preparation especially in combination with copper oxide. Zhao et al. reported the construction of CuO/$Cu_2O$@CoO core shell nanowire arrays by combining a chemical deposition method [43]. The results indicated the decoration of CuO/$Cu_2O$ nanowire core with branched CoO nanosheet shells. The as-obtained nanowire arrays demonstrated outstanding areal capacitance of 280 mF $cm^{-2}$ at a current density of 1 mA $cm^{-2}$ as well as superior cycling stability retaining 90.7% of the initial capacitance after 3000 cycles. The schematic illustration of the synthesis of Cu-Co nanowires contained four individual stages as displayed in Figure 4. The first step involves anodization of the Cu foil for preparing $Cu(OH)_2$ nanowire arrays followed by calcination step to form the CuO/$Cu_2O$ composite. It is then immerged into the $Co(NO_3)_2{\cdot}6H_2O$ and urea mixed solution to complete the deposition process in step three and annealing in argon in the final step.

Combination of nickel oxide and cooper oxide for synthesis of nanostructures can be used for high-performance supercapacitor preparation attracted. Nickel hydroxides (oxides) have become attractive pseudocapacitive materials due to low cost, environmental computability, facile synthesis, and high theoretical specific capacitance (3750 F $g^{-1}$). Various composites can be synthesized according to different mole ratios of CuO and NiO for achieving improved charge separation and hence synergistic results [44]. An integrated system combining solar cells with a hybrid supercapacitor was assembled by Boukherroub et al. for operating a homemade windmill device for achieving energy conversion, storage, and utilization using $Ni(OH)_2$@CuO@Cu electrode materials [45]. Cu foam current collector was used because of its three dimensional (3D) structure and good conductivity. The chemical oxidation process led to formation of CuO on Cu foam (CuO@Cu), followed by thermal annealing and electrodeposition of $Ni(OH)_2$ for preparing $Ni(OH)_2$@CuO@Cu electrode materials. Alteration of the time spans influenced the electrochemical properties of the resulting electrodes where among all electrodes, $Ni(OH)_2$@CuO@Cu-150 composite- 150 s of time span- exhibited the largest active surface area of 512.6 $cm^{-2}$. N-doped reduced graphene oxide coated on nickel foam (N-rGO/NF) was applied as a negative electrode, while $Ni(OH)_2$@-CuO@Cu-150 was used as positive electrode, and a a filter paper (separator) immersed into 2 M KOH aqueous solution was applied for preparing a hybrid supercapacitor with the largest areal capacity of 7063.2 mC $cm^{-2}$ at 20 mA $cm^{-2}$. The three-digit digital display was successfully lighten up by the supercapacitor

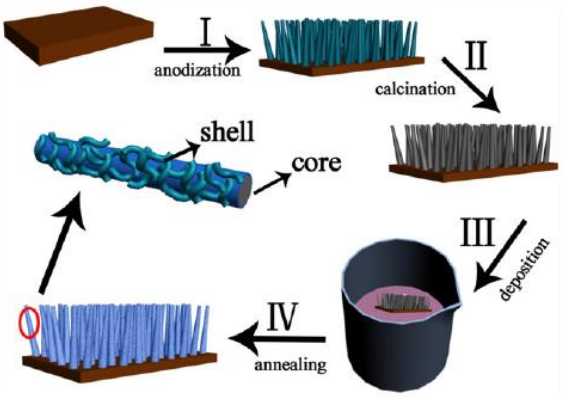


Figure 4. Synthesis of $CuO/Cu_2O$@CoO core shell nanowire arrays, (I) electrochemical anodization of Cu foil (II) calcination of $Cu(OH)_2$ nanowire (III) chemical bath deposition in 90 °C for 10 h (IV) annealing of the sample after chemical bath deposition process.

devices for 1 min and 28 s. Similarly, $Ni(OH)_2$@CuO core-shell nanowire arrays on 3D copper foams were reported by Sun et al. for high-performance asymmetric supercapacitors [46]. The electrochemical experiments revealed that the $Ni(OH)_2$@CuO electrode delivered large areal capacitance (1.625 F $cm^{-2}$ at 3 mA $cm^{-2}$), excellent rate capacity (1.285 F $cm^{-2}$ at 30 mA $cm^{-2}$), and excellent cycling stability (retaining 96.4% after 5000 cycles). Elsewhere, a hybrid NiO–CuO mesoporous nanowire array which constructs a three-dimensional (3D) hollow architecture via a facile hydrothermal method and subsequent annealing with abundant oxygen vacancies [47]. Five different samples of the NiO–CuO with different molar ratios of Ni : Cu were obtained among which the sample of NiO–CuO with Ni : Cu = 1:1. It showed an excellent electrochemical performance such as a high areal capacitance of 4.35 F $cm^{-2}$ and a large specific capacitance of 1450.8 F $g^{-1}$ at a current density of 2 mA $cm^{-2}$, outperforming the behavior of pure NiO and CuO.

Thin films constructed $Ni(OH)_2$/CuO nanocomposites in KOH solution were investigated and showed good electrochemical performances with a potential window between 0 and 0.5 V, plus a maximum specific capacitance of about 27 F $g^{-1}$ observed at a scan rate of 10 mV $s^{-1}$ delivering a specific capacitance of 29 F $g^{-1}$ [48]. The successful in-situ fabrication of ordered $CuO/Cu_2O$ nanosheet arrays on copper foil was reported for binder-free high-performance electrode materials [49]. The NiOOH for further modification of $CuO/Cu_2O$ arrays was introduced via a facile hydrothermal deposition treatment. The as-fabricated composite nanosheet arrays exhibited a brilliant areal capacitance of 1206 mF $cm^{-2}$ at a current density of 1 mA $cm^{-2}$ in KOH aqueous medium with an outstanding long-term cycling stability, with 84.6% of initial capacitance after 3000 charge/discharge cycles. The nickel foam was also used as skeleton for preparing nanostructures with potential to be used in high-performance supercapacitors.

CuO nanosheet arrays freely standing on nickel foam were prepared via a template-free growth method and formed a uniform film of around 5 μm in thickness [50]. The CuO exhibited the highest reported specific capacitance of 569 F $g^{-1}$ at a current density of 5m $Acm^{-2}$. Electrolyte concentration would exert a significant effect on the performance of CuO capacitance. Other hieratical CuO clusters based on nickel foams (CuO–Ni) were synthesized by Li et al. via the electroless copper plating and chemical etching process in KOH solution [51]. The prepared electrode was binder less and it bonded with the nickel collector properly, thus it enhanced electronic conductivity. In addition, the high alkali resistance of nickel substrate and hieratical nanostructure of CuO clusters were conducive to obtain excellent electrochemical performances. The specific areal capacitance of CuO–Ni electrode reached up to 1.61 F $cm^{-2}$ at 3 mA $cm^{-2}$ (equivalent to 679 F $g^{-1}$ at 1.27 A $g^{-1}$), and retains

93.6% after 5000 testing cycles, which is mainly attributed to its perfect hieratical structure and high electrical conductivity. The synthesis and application of Cu-plated nickel foam have been reported with products with different morphologies such as nanoflake network [52], nanosheets [53], nanoflower [54], and necklace-like [55]. These structures across with good specific areal capacitance and high electrical conductivity resulted to the synthesized copper oxide-nickel oxide-based materials as suitable candidate in preparation of electrochemical supercapacitors. The reported synthesis of CuO nanosheets on nickel foam by Xiaoli He et al. involved utilizing ZnO nanowires for high-performance supercapacitor preparation [17]. ZnO was applied on nickel substrates to increase the surface area. Figure 5 illustrates the detailed preparation pathway in which ZnO nanowires were grown on the Ni substrate using the hydrothermal method. A layer of $Cu(NO_3)_2$ formed on the ZnO surface by dissolving a Cu foil.

Potassium nitrate and depositing Cu electrochemically using the CV technique. Subsequently, blue-colored $Cu(OH)_2$ nanosheets were obtained by immersing the as-prepared substrate in KOH solution. The transformation of $Cu(OH)_2$ to CuO was the last step in this process carried out through simple calcination at 175°C for 30 min.

The increase in the current density affected the specific capacitance in the way that the maximum capacitance (545 F $g^{-1}$) was observed at a current density of 1 A $g^{-1}$, confirming the excellent capacity for charge storage. In addition, cyclic charge/discharge process at a current density of 7 A $g^{-1}$ was applied to determine the cycling performance of the amorphous CuO nanosheet electrode with the result confirming that after 2000 cycles, the electrode with an initial capacitance of 430 F $g^{-1}$, still maintained a large capacitance of 370 F $g^{-1}$, indicating a good cyclic stability.

The influence of silver dope on electrochemical behaviors of CuO nanosheet arrays was investigated by Wang et al. [56]. It seems that the presence of dispersed Ag particle coated the CuO nanosheet arrays can improve the electrode capacitance in comparison with the unmodified CuO nanosheet arrays. Nickel foam was used as a substrate in this report which was covered with a thick and uniform film of CuO. The immersion of the as-prepared electrode in ethanolic solution of $[Ag(NH_3)_2]^+$ and polyvinylpyrrolidone led to the formation of Ag-doped CuO electrode. The Ag particle could facilitate fast electron transport between the current collectors and the active materials. The reported specific capacitance of the electrode was 689 F $g^{-1}$ at 1 A $g^{-1}$ and 299 F $g^{-1}$ at 10 A $g^{-1}$, respectively. A hybrid electrode composed of conductive Ag flakes grown on CuO nanorods via in-situ chemical approach was prepared for the first time recently [57]. The electrode demonstrated a superior specific capacitance of 812 F $g^{-1}$ at a current density of 2 A $g^{-1}$ which is retained of about 110.37% after 5000 cycles. Copper foam was used as substrate for $Cu(OH)_2$ nanorods growth and further conversion into CuO nanorods through heat-treatment at 200°C. In order to avoid oxidation of Cu slices, the entire process was carried out under nitrogen atmosphere. Then, the as-prepared CuO@Cu slice was immersed in $AgNO_3$ solution at room temperature and only for 120 s, which led to synthesis of the flake-like Ag in response to spontaneous reaction on CuO surface.

Rare earth elements (lanthanides) with special electronic structures have unique optical, electronic, and magnetic properties so they can be doped to nanomaterials to enhance their electrical, electrochemical, magnetic, and semiconducting properties as compared to pure and undoped nanomaterials. $Sm_2O_3$ is one of the rare earth compounds with high surface basicity, fast oxygen ion mobility, and interesting catalytic properties. $Sm_2O_3$ modified CuO nanoflowers were prepared via a simple chemical precipitation-hydrothermal method [58]. A homogeneous solution of copper and samarium nitrate was used for synthesizing hierarchical structured $Sm_2O_3$ modified CuO nanoflowers. The results indicated that the specific capacitances of $Sm_2O_3$ modified CuO-based electrode increased by four times upon serving as supercapacitor electrode materials at current density of 5.0 A $g^{-1}$ where the charge transfer resistance of $Sm_2O_3$ modified CuO-based electrode decreased. It was shown that the electrode possessed the highest specific capacitance in all prepared materials at current density of 0.5 A $g^{-1}$, with nearly 84.6% retention capacitance over 2000 cycles at 1.0 A $g^{-1}$.

The $Cu_2O$ reverse cubic heterostructures prepared via hydrothermal method was used for preparing CuO–

$SnO_2$ reverse cubic heterojunctions through reaction with various amounts of $SnCl_2.2H_2O$ [59]. The chemical equation is as follows:

$$2\,Cu_2O + 4\,Sn^{2+} + 8\,OH^- + 3\,O_2 \rightarrow 4\,CuO - SnO_2 + 4\,H_2O \quad (5)$$

The morphology of CuO-$SnO_2$ samples revealed that the reverse cubic heterojunction has a relative uniform distribution. The enlarged SEM images of the samples indicating a six-side reverse cubic structures for products with the size of the sample being about 7–8 mm. The unique six-side reverse cubic structure is critical to the electrochemical performance of this material. A parabolic trend was presented between the specific capacitance of CuO–$SnO_2$ and increasing $SnO_2$ content. The CuO–$SnO_2$ heterojunctions manifested a high specific capacitance of 1972 F $g^{-1}$ at 1 A $g^{-1}$ and outstanding cycling stability. The higher specific capacitance of the pure CuO–$SnO_2$ heterojunctions was mainly associated to the high conductivity improved by the high electron hole state in the heterojunctions. The electron effective and hole effective mass of CuO–$SnO_2$ heterojunctions were calculated where the high value of hole effective mass was the main reason for the high specific capacitance of CuO–$SnO_2$ heterojunctions. The asymmetric supercapacitor made using the CuO-9 wt% $SnO_2$ heterojunction demonstrated a remarkable energy density of 117.32 W h $kg^{-1}$ at a power density of 13 624.26 W $kg^{-1}$. Also note that even at a high power density of 36 663.16 W $kg^{-1}$, the energy density could reach 96.75 W h $kg^{-1}$.

## 6. Cu based nanocomposite electrode materials

Double hydroxide nanostructures compounds are promising electrode materials for supercapacitors thanks to their facile accessibility to active sites and high electrical conductivity. In order to take advantage of these properties, heterostructures based on nickel have been designed with some transition metals such as Mn, Fe, Co, and Mo. These heterostructures in combination with copper oxide have been used for application in high-performance supercapacitor electrodes. In addition, ultrathin layered double hydroxide nanosheets (LDHs) which are promising candidates as electrode materials for energy storage have also been used for synthesis of hierarchical structures. A hierarchical NiMn-LDH@CuO/CF core-shell heterostructure comprised of a vertical and intercrossing ultrathin NiMn-LDHs nanosheets shell and a slightly curly and tops tangled CuO nanowires core. The prepared electrode exhibited a high areal capacitance of 6077 mF $cm^{-2}$ (2430.8 F $g^{-1}$) at a current density of 2 mA $cm^{-2}$ (0.8 A $g^{-1}$) [60]. The solid-state asymmetric supercapacitor device based on the hierarchical NiMn-LDH@CuO/CF core-shell material was used as positive electrode in combination of activated carbon as negative electrode exhibited an energy density of 10.8Wh $kg^{-1}$ at a power density of 100W$kg^{-1}$. The synthesis initiated with preparation of CuO nanowires on copper foam via a simple calcination process followed by a hydrothermal strategy step using CuO nanowires as template. The hierarchical heterostructure provided a high specific surface area which could enhance the number of active sites and promote the charge transfer as well as redox reactions during electrochemical applications. The SEM image revealed that the utilized Cu foam was covered with crossed $Cu(OH)_2$ nanorods after the wet-oxidation process and the Cu foam remained the 3D grid structure. After the calcination treatment, $Cu(OH)_2$ nanorods were converted into CuO nanowires and formed bunch-like nanowire arrays. The as-prepared electrode exhibited excellent cycling stability of 89.22% retention after 8000 cycles and possessed the ability to lighten up a blue LED indicator for 8 min.

A hierarchical core–shell nanorod array consisting of layered Ni–Fe double hydroxide nanosheets shell and CuO nanorods core was synthesized on the copper foam substrate and used directly as binder-free electrodes for high-performance supercapacitors [61]. This structure has several merits such as providing numerous redox reaction active sites, short ion diffusion pathways, low equivalent series resistance, and low structural impact during charging and discharging processes as well as synergistic effect between the CuO@Ni–Fe LDH hierarchical core–shell nanorods arrays and the Cu foam substrate.

Accordingly, high specific capacitance of 2.682 F $cm^{-2}$, good coulombic efficiency (82.7% at 2 mA $cm^{-2}$), good rate capability, and good stability with 86.67% capacitance retention were obtained after 5000

cycles. $CuO@Co_xNi1-_x(OH)_2$ nanowire arrays on copper foam were reported by Hui et al. in preparing long-life supercapacitors [62]. Cobalt was also used in synthesis of ultra-thin cobalt-nickel layered double hydroxide onto the core of 3D CuO cross-linked nanosheet [63]. The preparation of the ternary transition metal oxides exhibited superior properties in this area where Mo-based structures were considered as a suitable candidate for electrode materials. Elsewhere, the synthesis of ternary heterostructure based on CuO and molybdenum oxide was reported [64] and employed in high-performance supercapacitor electrode preparation. Cu foam was used as substrate for obtaining the CuO nanorods with chemical bath deposition. Subsequently, the multi-dimensional $CoMoO_4$/CuO heterostructure was grown on the as-prepared CuO nanorods via the hydrothermal procedure with the obtained nanostructure utilized as a binder-free supercapacitor electrode. In this report, they used a two-step synthesis pathway to obtain the final nanocomposite electrode. Initially, CuO nanorods were synthesized on Cu foam using chemical bath deposition and then the product was placed into an aqueous homogeneous mixture containing $Na_2MoO_4$. $2H_2O$ and $Co(NO_3)_2.6H_2O$ and kept at autoclave in 180°C. The XRD peaks confirmed the formation of CuO on Cu foam and $CoMoO_4$ planes. The dense and homogeneous nanocomposite was revealed in SEM images. The 2D $CoMoO_4$ nanosheets and 1D CuO nanorods acted as a base for $CoMoO_4$/CuO nanostructure to form stereoscopic and an open multi-dimensional nanostructure with excellent electrochemical performance for supercapacitor. $CoMoO_4$/CuO electrode delivered specific capacitance of 1176 F $g^{-1}$ at the scan rate of 1 mV $s^{-1}$ and excellent cycle stability of 95.1% over 5000 cycles under the current density of 2.5 A $g^{-1}$ with energy density about 67.01 Wh $kg^{-1}$. Similarly, Mo-doped CuO nanosheets on Ni foams were reported recently with specific capacitance of 1392 F $g^{-1}$ at 2 A $g^{-1}$ [65]. The electrode maintained approximately 76% of the initial specific capacitance after 10,000 cycles. In addition, an asymmetric Mo-doped CuO nanosheets cell was assembled and could deliver a considerably high energy density of 36 W h $kg^{-1}$ at 810 W $kg^{-1}$ and exhibited an outstanding cycling stability with 81% capacitance retention for over 5000 cycles where two as-prepared electrodes in series could lighten a red LED.

## 7. Conclusion and future prospective

The progressive development of electrochemical supercapacitors is essential for energy storage purposes. In this review, a detailed description of the recent developments of electrode materials based on copper oxides and their composites materials has been given. The authors believe that more research should be focused on different nanocomposite materials made up of CuO, such as emerging two-dimensional nanoflakes, for fabricating high-performance supercapacitors electrodes. Continuous research is needed to allow these materials and novel devices to meet the growing energy demands. Also, it is essential to make progress in synthesis parameters and material properties for full capability exploration of the supercapacitor electrode materials. The energy storage mechanism of CuO materials has also become increasingly clear regarding the advancement of advanced characterization technologies, and more research efforts are needed in this area. In addition, the improvement of the reaction temperature range, long lifetime, self-discharge rate, long lifetime, and the degradation of supercapacitor component should be vigorously investigated for improving overall cell performance. Energy storage devices has become a critical issue in both electrochemical and mechanical aspects, so modification methods is needed to improve the pore structures, electrical conductivity, and electrochemical activity of them. The current approaches of designing electrode materials for supercapacitors are in their promising phase and needs more attention to explore them holistically. In addition, research is now being focused on the production of multifunctional energy storage devices with different properties of auto-healing, great sensing, heat or pressure, automated charging mode under light, etc. So, backing an uninterrupted energy source is essential especially in the biomedical, military, installed astronomical and automated industrial electronic tools. However, a massive packet of challenges desires instant solutions and an enormous work for the researchers to figure out smart materials for emerging supercapacitor devices that may tremendously act as the most reliable mode for everlasting and maintainable energy sources.

## 8. References


1.R. Wang, M. Yao, Z. Niu, Smart supercapacitors from materials to devices, InfoMat, 113-125, 2 (2020).

2.D. Majumdar, S. Ghosh, Recent advancements of copper oxide based nanomaterials for supercapacitor applications, Journal of Energy Storage, 101995, 34 (2021).

3.D. Larcher, J.-M. Tarascon, Towards greener and more sustainable batteries for electrical energy storage, Nature chemistry, 19-29, 7 (2015).

4.T.A. Mamvura, G.S. Simate, The potential application of graphene nanotechnology for renewable energy systems, Graphene-Based Nanotechnologies for Energy and Environmental Applications, Elsevier2019, pp. 59-80.

5.Y. Wang, Y. Song, Y. Xia, Electrochemical capacitors: mechanism, materials, systems, characterization and applications, Chemical Society Reviews, 5925-5950, 45 (2016).

6.M. Gusain, P. Singh, Y. Zhan, Energy Storage Devices (Supercapacitors and Batteries), Advances in Hybrid Conducting Polymer Technology, Springer2021, pp. 53-75.

7.S. Sagadevan, A. Marlinda, Z.Z. Chowdhury, Y.B.A. Wahab, N.A. Hamizi, M. Shahid, F. Mohammad, J. Podder, M.R. Johan, Fundamental electrochemical energy storage systems, Advances in Supercapacitor and Supercapattery, Elsevier2021, pp. 27-43.

8.S. Zhu, M. Wu, M.-H. Ge, H. Zhang, S.-K. Li, C.-H. Li, Design and construction of three-dimensional CuO/polyaniline/rGO ternary hierarchical architectures for high performance supercapacitors, Journal of Power Sources, 593-601, 306 (2016).

9.W. He, C. Wang, F. Zhuge, X. Deng, X. Xu, T. Zhai, Flexible and high energy density asymmetrical supercapacitors based on core/shell conducting polymer nanowires/manganese dioxide nanoflakes, Nano Energy, 242-250, 35 (2017).

10.M. Abdel Maksoud, R.A. Fahim, A.E. Shalan, M. Abd Elkodous, S. Olojede, A.I. Osman, C. Farrell, A.a.H. Al-Muhtaseb, A. Awed, A. Ashour, Advanced materials and technologies for supercapacitors used in energy conversion and storage: a review, Environmental Chemistry Letters, 375-439, 19 (2021).

11.M. Mustaqeem, G.A. Naikoo, F. Rahimi, M.Z. Pedram, H. Pourfarzad, I.U. Hassan, F. Arshad, Y.-F. Chen, Rational design of Cu based composite electrode materials for high-performance supercapacitors–A review, Journal of Energy Storage, 104330, 51 (2022).

12.J.B. Goodenough, Electrochemical energy storage in a sustainable modern society, Energy & Environmental Science, 14-18, 7 (2014).

13.G. Zhou, L. Xu, G. Hu, L. Mai, Y. Cui, Nanowires for electrochemical energy storage, Chemical reviews, 11042-11109, 119 (2019).

14.W. Xu, S. Dai, G. Liu, Y. Xi, C. Hu, X. Wang, CuO nanoflowers growing on carbon fiber fabric for flexible high-performance supercapacitors, Electrochimica Acta, 1-8, 203 (2016).

15.R.K. Sahoo, A. Das, K. Samantaray, S.K. Singh, R.S. Mane, H.-C. Shin, J.M. Yun, K.H. Kim, Electrochemical glucose sensing characteristics of two-dimensional faceted and non-faceted CuO nanoribbons, CrystEngComm, 1607-1616, 21 (2019).

16.P. Subalakshmi, A. Sivashanmugam, CuO nano hexagons, an efficient energy storage material for Li-ion battery application, Journal of Alloys and Compounds, 523-531, 690 (2017).

17.X. He, J. Bae, Facile synthesis of amorphous CuO nanosheets on nickel foam by utilizing ZnO nanowires for high-performance supercapacitors, Journal of Electronic Materials, 5468-5476, 47 (2018).

18.K. Ganesan, A. Amaliroselin, I. Joseph Panneer Doss, N. Anandhan, R. Ramesh, S. Prabhu, G. Sivakumar, R. Panneerselvam, High-performance energy storage of highly saturated ferromagnetic cobalt-doped cuprous oxide thin films, Journal of Materials Science: Materials in Electronics, 7509-7527, 32 (2021).

19.Y. Li, S. Chang, X. Liu, J. Huang, J. Yin, G. Wang, D. Cao, Nanostructured CuO directly grown on copper foam and their supercapacitance performance, Electrochimica Acta, 393-398, 85 (2012).

20.Q. Zhang, K. Zhang, D. Xu, G. Yang, H. Huang, F. Nie, C. Liu, S. Yang, CuO nanostructures: synthesis, characterization, growth mechanisms, fundamental properties, and applications, Progress in Materials Science, 208-337, 60 (2014).

21.S. Anandan, G.-J. Lee, J.J. Wu, Sonochemical synthesis of CuO nanostructures with different morphology, Ultrasonics sonochemistry, 682-686, 19 (2012).

22.X. Shu, Y. Wang, J. Cui, G. Xu, J. Zhang, W. Yang, M. Xiao, H. Zheng, Y. Qin, Y. Zhang, Supercapacitive performance of single phase CuO nanosheet arrays with ultra-long cycling stability, Journal of Alloys and Compounds, 731-739, 753 (2018).

23.H. Nan, W. Ma, Q. Hu, X. Zhang, Copper oxide nanofilm on 3D copper foam as a novel electrode

material for supercapacitors, Applied Physics A, 1451-1457, 119 (2015).
24. Y.-K. Hsu, Y.-C. Chen, Y.-G. Lin, Characteristics and electrochemical performances of lotus-like CuO/Cu (OH) 2 hybrid material electrodes, Journal of Electroanalytical Chemistry, 43-47, 673 (2012).
25. A. Pendashteh, M.S. Rahmanifar, M.F. Mousavi, Morphologically controlled preparation of CuO nanostructures under ultrasound irradiation and their evaluation as pseudocapacitor materials, Ultrasonics sonochemistry, 643-652, 21 (2014).
26. D. He, S. Xing, B. Sun, H. Cai, H. Suo, C. Zhao, Design and construction of three-dimensional flower-like CuO hierarchical nanostructures on copper foam for high performance supercapacitor, Electrochimica Acta, 639-645, 210 (2016).
27. X. Su, G. Feng, L. Yu, Q. Li, H. Zhang, W. Song, G. Hu, In-situ green synthesis of CuO on 3D submicron-porous/solid copper current collectors as excellent supercapacitor electrode material, Journal of Materials Science: Materials in Electronics, 3545-3551, 30 (2019).
28. L. Kunhikrishnan, R. Shanmugam, A facile route to synthesize CuO sphere-like nanostructures for supercapacitor electrode application, Journal of Materials Science: Materials in Electronics, 21528-21539, 31 (2020).
29. P. Subalakshmi, M. Ganesan, A. Sivashanmugam, Synthesis of 3D architecture CuO micro balls and nano hexagons and its electrochemical capacitive behavior, Materials & Design, 104-112, 119 (2017).
30. S.K. Shinde, D.P. Dubal, G.S. Ghodake, D.Y. Kim, V.J. Fulari, Morphological tuning of CuO nanostructures by simple preparative parameters in SILAR method and their consequent effect on supercapacitors, Nano-Structures & Nano-Objects, 5-13, 6 (2016).
31. A.C. Nwanya, D. Obi, K.I. Ozoemena, R.U. Osuji, C. Awada, A. Ruediger, M. Maaza, F. Rosei, F.I. Ezema, Facile synthesis of nanosheet-like CuO film and its potential application as a high-performance pseudocapacitor electrode, Electrochimica Acta, 220-230, 198 (2016).
32. S. Shinde, D. Dubal, G. Ghodake, D. Kim, V. Fulari, Nanoflower-like CuO/Cu (OH) 2 hybrid thin films: Synthesis and electrochemical supercapacitive properties, Journal of Electroanalytical Chemistry, 80-85, 732 (2014).
33. M.R. Das, A. Mukherjee, P. Maiti, S. Das, P. Mitra, Studies on multifunctional properties of SILAR synthesized CuO thin films for enhanced supercapacitor, photocatalytic and ethanol sensing applications, Journal of Electronic Materials, 2718-2730, 48 (2019).
34. Z. Komeily-Nia, M. Montazer, B. Nasri-Nasrabadi, A practical approach to load CuO/MnO2 core/shell nanostructures on textiles through in situ wet chemical synthesis, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 123998, 583 (2019).
35. Z. Zhang, C. Ma, M. Huang, F. Li, S. Zhu, C. Hua, L. Yu, H. Zheng, X. Hu, Y. Zhang, Birnessite MnO2-decorated hollow dandelion-like CuO architectures for supercapacitor electrodes, Journal of Materials Science: Materials in Electronics, 4212-4220, 26 (2015).
36. M. Huang, Y. Zhang, F. Li, Z. Wang, N. Hu, Z. Wen, Q. Liu, Merging of Kirkendall growth and Ostwald ripening: CuO@ MnO2 core-shell architectures for asymmetric supercapacitors, Scientific reports, 1-9, 4 (2014).
37. H. Xie, X. Liu, R. Wu, J. Liu, J. Wu, L. Li, High-Performance Supercapacitor with Faster Energy Storage and Long Cyclic Life Based on CuO@ MnO2 Nano-Core–Shell Array on Carbon Fiber Surface, ACS Applied Energy Materials, 7325-7334, 3 (2020).
38. Y. Zhang, W.W. Guo, T.X. Zheng, Y.X. Zhang, X. Fan, Engineering hierarchical Diatom@ CuO@ MnO2 hybrid for high performance supercapacitor, Applied Surface Science, 1158-1165, 427 (2018).
39. Y.X. Zhang, F. Li, M. Huang, One-step hydrothermal synthesis of hierarchical MnO2-coated CuO flower-like nanostructures with enhanced electrochemical properties for supercapacitor, Materials letters, 203-206, 112 (2013).
40. M. Mandal, R. Nagaraj, K. Chattopadhyay, M. Chakraborty, S. Chatterjee, D. Ghosh, S.K. Bhattacharya, A high-performance pseudocapacitive electrode based on CuO–MnO2 composite in redox-mediated electrolyte, Journal of Materials Science, 3325-3335, 56 (2021).
41. G. Durai, P. Kuppusami, K. Viswanathan, Investigation on microstructure and improved supercapacitive performance of Mn doped CuO thin films prepared by reactive radio frequency magnetron sputtering, Journal of Materials Science: Materials in Electronics, 2051-2058, 29 (2018).
42. N. Ghassemi, S.S.H. Davarani, H.R. Moazami, Cathodic electrosynthesis of CuFe2O4/CuO composite nanostructures for high performance supercapacitor applications, Journal of Materials Science: Materials in Electronics, 12573-12583, 29 (2018).
43. J. Zhao, X. Shu, Y. Wang, C. Yu, J. Zhang, J. Cui, Y. Qin, H. Zheng, J. Liu, Y. Zhang, Construction of CuO/Cu2O@ CoO core shell nanowire arrays for

high-performance supercapacitors, Surface and Coatings Technology, 15-21, 299 (2016).
44. Y. Yuan, X. Xia, J. Wu, J. Yang, Y. Chen, S. Guo, Nickel foam-supported porous Ni (OH) 2/NiOOH composite film as advanced pseudocapacitor material, Electrochimica Acta, 2627-2632, 56 (2011).
45. M. Li, A. Addad, P. Roussel, S. Szunerits, R. Boukherroub, High performance flexible hybrid supercapacitors based on nickel hydroxide deposited on copper oxide supported by copper foam for a sunlight-powered rechargeable energy storage system, Journal of Colloid and Interface Science, 520-530, 579 (2020).
46. L.n. Xu, H. Zhang, J. Li, X. Guo, H. Sun, Y.a. Li, T. Wu, Designing core-shell Ni (OH) 2@ CuO nanowire arrays on 3D copper foams for high-performance asymmetric supercapacitors, ChemElectroChem, 5462-5468, 6 (2019).
47. Z. Fang, S. ur Rehman, M. Sun, Y. Yuan, S. Jin, H. Bi, Hybrid NiO–CuO mesoporous nanowire array with abundant oxygen vacancies and a hollow structure as a high-performance asymmetric supercapacitor, Journal of Materials Chemistry A, 21131-21142, 6 (2018).
48. D. Iwueke, C. Amaechi, A. Nwanya, A. Ekwealor, P. Asogwa, R. Osuji, M. Maaza, F. Ezema, A novel chemical preparation of Ni (OH) 2/CuO nanocomposite thin films for supercapacitive applications, Journal of Materials Science: Materials in Electronics, 2236-2242, 26 (2015).
49. X. Shu, Y. Wang, Y. Qin, C. Yu, J. Zhang, J. Zhao, J. Cui, L. Cui, H. Zheng, Y. Zhang, Synthesis and supercapacitive performance of CuO/Cu2O nanosheet arrays modified by hydrothermal deposited NiOOH, Journal of Solid State Electrochemistry, 1489-1497, 21 (2017).
50. G. Wang, J. Huang, S. Chen, Y. Gao, D. Cao, Preparation and supercapacitance of CuO nanosheet arrays grown on nickel foam, Journal of Power Sources, 5756-5760, 196 (2011).
51. H. Sun, J. Li, T. Wu, F. Yu, X. Guo, H. Zhang, Hieratical CuO clusters in-situ grown on copper films coated three-dimensional nickel foams for high-performance supercapacitors, Ceramics International, 17461-17468, 46 (2020).
52. K. Malaie, M. Ganjali, T. Alizadeh, P. Norouzi, Simple electrochemical preparation of nanoflake-like copper oxide on Cu-plated nickel foam for supercapacitor electrodes with high areal capacitance, Journal of Materials Science: Materials in Electronics, 14631-14637, 28 (2017).
53. Y. Guo, X. Hong, Y. Wang, Q. Li, J. Meng, R. Dai, X. Liu, L. He, L. Mai, Multicomponent hierarchical Cu-doped NiCo-LDH/CuO double arrays for ultralong-life hybrid fiber supercapacitor, Advanced Functional Materials, 1809004, 29 (2019).
54. L. Arun, C. Karthikeyan, D. Philip, M. Sasikumar, E. Elanthamilan, J.P. Merlin, C. Unni, Effect of Ni2+ doping on chemocatalytic and supercapacitor performance of biosynthesized nanostructured CuO, Journal of Materials Science: Materials in Electronics, 21180-21193, 29 (2018).
55. S.H. Xu, G.T. Fei, H.M. Ouyang, G.L. Shang, X.D. Gao, L.D. Zhang, Necklace-like NiO-CuO heterogeneous composite hollow nanostructure: preparation, formation mechanism and structure control, Scientific reports, 1-13, 7 (2017).
56. J. Huang, H. Wu, D. Cao, G. Wang, Influence of Ag doped CuO nanosheet arrays on electrochemical behaviors for supercapacitors, Electrochimica Acta, 208-212, 75 (2012).
57. Y. Mao, Y. Qian, L. Li, Y. Li, J. Xie, W. Hu, Novel Ag configurations decorated CuO hybrid electrode for high-performance asymmetric supercapacitor, Journal of Materials Science, 6963-6975, 55 (2020).
58. X. Zhang, M. He, P. He, H. Liu, H. Bai, J. Chen, S. He, X. Zhang, F. Dong, Y. Chen, Hierarchical structured Sm2O3 modified CuO nanoflowers as electrode materials for high performance supercapacitors, Applied Surface Science, 933-943, 426 (2017).
59. M. Chuai, X. Chen, K. Zhang, J. Zhang, M. Zhang, CuO–SnO 2 reverse cubic heterojunctions as high-performance supercapacitor electrodes, Journal of Materials Chemistry A, 1160-1167, 7 (2019).
60. A. Zhang, W. Zheng, Z. Yuan, J. Tian, L. Yue, R. Zheng, D. Wei, J. Liu, Hierarchical NiMn-layered double hydroxides@ CuO core-shell heterostructure in-situ generated on Cu (OH) 2 nanorod arrays for high performance supercapacitors, Chemical Engineering Journal, 122486, 380 (2020).
61. G. Liu, X. He, D. He, B. Cui, L. Zhu, H. Suo, C. Zhao, Construction of CuO@ Ni–Fe layered double hydroxide hierarchical core–shell nanorods arrays on copper foam for high-performance Supercapacitors, Journal of Materials Science: Materials in Electronics, 2080-2088, 30 (2019).
62. S. Wu, H. Guo, K. San Hui, K.N. Hui, Rational design of integrated CuO@ CoxNi1− x (OH) 2 nanowire arrays on copper foam for high-rate and long-life supercapacitors, Electrochimica Acta, 759-768, 295 (2019).
63. F. Chen, C. Chen, Q. Hu, B. Xiang, T. Song, X. Zou, W. Li, B. Xiong, M. Deng, Synthesis of CuO@ CoNi LDH on Cu foam for high-performance supercapacitors, Chemical Engineering Journal, 126145, 401 (2020).

64. F. Liu, Y. Yang, S. Li, T. Chen, H. Long, H. Wang, M. Liu, Multi-dimensional CuO nanorods supported CoMoO4 nanosheets heterostructure as binder free and high stable electrode for supercapacitor, Journal of Materials Science: Materials in Electronics, 10353-10361, 29 (2018).

65. W. Lv, L. Li, Q. Meng, X. Zhang, Molybdenum-doped CuO nanosheets on Ni foams with extraordinary specific capacitance for advanced hybrid supercapacitors, Journal of Materials Science, 2492-2502, 55 (2020).