

NANOSTRUCTURED CuO ELECTRODES FOR SUPERCAPACITORS - A SUCCINCT REVIEW

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ABSTRACT

Supercapacitors (SC), which are specialized form of capacitors with an exceedingly high level of capacitance are the scientific and technological evolution of conventional capacitors towards electrochemical batteries. Electrodes, which are the primary components for energy storage and delivery, ultimately determine the overall performance of a supercapacitor. Many efforts in the research of numerous electrode materials and methods for their synthesis have been made in recent years to increase the energy storage density of supercapacitors. In this review, an overview of the types of supercapacitors and various electrode materials like carbon based materials, metal oxides and conducting polymers have been reported in brief. Notable research examples have been highlighted through extensive analysis of the literature to present the progress to date for the use of nanostructured copper oxide (CuO) based electrodes for supercapacitors with focus on the energy storage capability.

Keywords: Supercapacitors, electrode materials, energy storage, nanostructures, CuO electrode

1. INTRODUCTION

Providing sufficient energy to meet the requirements of a growing world population with rising living standards will require major advances in energy supply and efficiency. A confluence of industrial, social, environmental and economic factors and the evolving demands of modern society for a variety of applications has created much interest in electric energy storage systems (ESS). One of the great challenges for today's information-rich society is providing high-efficient, low-cost, and eco-friendly electrochemical energy conversion and storage devices for powering an increasingly diverse variety of applications.

As energy storage devices, supercapacitors store energy directly as charge on the electrode surface or sub-surface layer by simply electrostatic charge transfer, while batteries store energy in the bulk material by means of chemical reactions. Due to that fundamental difference between the systems, batteries provide higher energy density, but suffer from low power density and poor cycle life, whereas, SCs have the ability to store or release large quantities of energy in a very short

time period which is the basis for their high power density.

Since SCs combine the energy storage properties of batteries with the power discharge characteristics of capacitors, they possess attractive features such as high power density, faster charge-discharge cycling, long cycle life, zero maintenance, environment friendly nature, enhanced safety and better endurance. These characteristics make SCs to offer an attractive power solution for an increasing number of applications, like development of hybrid electric vehicles to meet high capacity and high power to satisfy the requirements for mileage and speed, power devices and systems, consumer electronics, cell phone base stations, digital cameras, aircraft and smart grids [1].

However, the major challenges for SCs are their insufficient energy density and high cost, which limits their more extensive applications. To realize the potential of SCs, it is important that they have to provide enhanced energy density without compromise in their inherent high power density and excellent cyclability.

The energy density (E) can be obtained by the total capacitance (C) and the operating voltage (V) based on the following equation.

$$E = \frac{1}{2} CV^2 \quad (1)$$

It is obvious that the energy density can be improved either by increasing the total capacitance or by increasing the operating voltage. To improve the total capacitance, the most intensive approaches include the discovery of advanced electrode materials and the improved understanding of ion transport mechanism in small pores. Moreover, selection of an appropriate electrolyte can greatly improve the operating voltage which contributes for the enhanced energy density.

Proper selection, design and fabrication of electrode materials, as well as the dynamic processes at the interfaces between electrodes and electrolytes, are essential for supercapacitors to operate efficiently. The properties of the active electrode materials, including surface area, pore size, pore connectivity, electrical conductivity and surface chemistry play a crucial role in determining the ultimate performance of a supercapacitor [2].

2. CLASSIFICATION OF SUPERCAPACITORS

Based on the energy storage mechanisms and active electrode materials used, supercapacitors can be divided into three categories, namely Electrochemical Double-Layer Capacitors (EDLCs), pseudo-capacitors (or redox capacitors) and hybrid capacitors [3]. A simplified classification of electrode materials

for different types of supercapacitors is shown in fig.1.

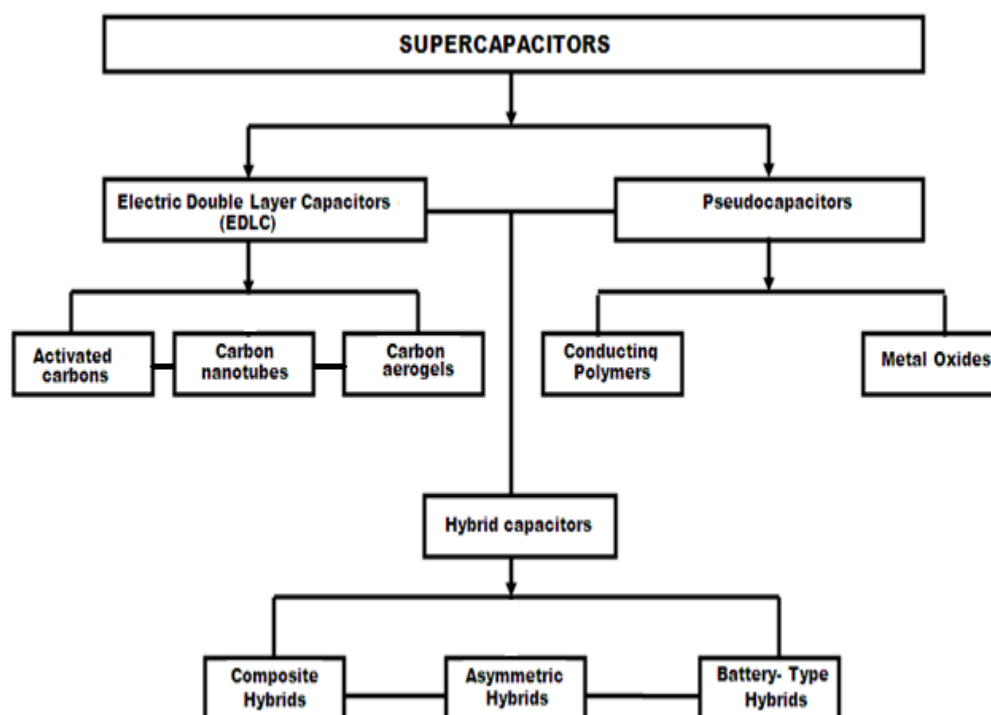


Figure 1 Different forms of supercapacitors and electrode materials

The literature refers to the group of electrochemical capacitors using non-faradaic accumulation of electrostatic charge at the electrode-electrolyte interface as Electrochemical Double-Layer Capacitors or EDLCs. Fast faradaic charge -transfer brought about by the charging of the electrical double-layer at the electrode-electrolyte interface determines the working of pseudocapacitors. The electrochemical capacitors that exhibit high capacitance utilizing both physical and chemical charge storage mechanisms are referred to as hybrid

supercapacitors. These capacitors attempt to exploit the best features of Electric Double Layer Capacitors (EDLCs) and pseudocapacitors to optimize the power density of EDLC with the energy density of a pseudocapacitor.

3. ELECTRODE MATERIALS

Based on energy storage mechanisms, three different kinds of electrode materials are exploited for supercapacitor applications. These include carbon based materials, conducting polymers and Transition Metal Oxides (TMOs). As electrode materials are

vital components in determining the electrochemical performance of a supercapacitor system, efforts were made to develop this kind of functional materials with higher specific capacitance to get maximum power density supercapacitors.

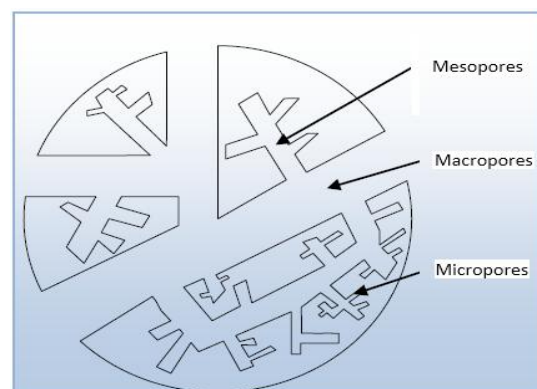
3.1 Carbon Based Materials

Carbon based materials are widely used as the electrode material in majority of commercially available EDLCs, as they possess key qualities like high conductivity, high specific surface area range ($1-3000 \text{ m}^2 \text{ g}^{-1}$), good corrosion resistance, environmental benignity, higher processability, temperature stability, higher working voltage (4-5 V), tunable pore structure, relatively low cost and compatibility with other materials in composites. Further, by various synthetic strategies, carbon can be tailored in different structures from bulk to nano regime. Activated carbon, carbon aerogels, carbon cryogels, carbon nanofibers, carbon nanotubes and graphene are the various forms of carbon which are exploited as electrode materials for SCs.

3.1.1 Activated carbon

The method of increasing the surface area and porosity of carbons by thermal or chemical treatment is called as “activation” which results in the formation of Activated

Carbon (AC). Naturally, the surface properties, electrical conductivity, porous system and Specific Surface Area (SSA) are of significant importance to the electrochemical behaviour of an active carbon electrode. Porous ACs possess a widely distributed pore sizes (Fig. 2) namely, micropores ($< 2 \text{ nm}$), mesopores (2-50 nm) and macropores ($> 50 \text{ nm}$).



(Source: Patrice Simon, 2008)

Figure 2 Types of pores in activated carbon

In general, higher SSA can accumulate a larger amount of the electrolyte at the electrode-electrolyte interface which possibly leads to a larger capacitance. But, in fact, sometimes it is found that the higher SSA carbon possesses less capacitance, the reason being the less efficient utilization of the much-narrowed micropores ($< 0.7 \text{ nm}$) due to the ion sieving effect. Moreover, excessive SSA leads to very low density for carbon which creates low conductivity and packing efficiency.

The energy density of AC based supercapacitors is about 4-5 Whkg⁻¹ while the specific capacitance reaches 100-120 Fg⁻¹ in organic electrolytes and 150-300 Fg⁻¹ in aqueous electrolytes, as reported [4]. The lower capacitance in the organic electrolytes is due to the fact that ions in the organic electrolyte are larger than the ions in an aqueous solvent, making micro pores in the AC unable to store charges anymore which limits the capacitance and energy density of supercapacitors [5]. Thus, the performance of supercapacitors using activated carbon electrodes is not only related to the surface area but also to the pore size distribution. To solve this drawback in ACs, controlled generation of pores with a narrow distribution in mesopores range was investigated [6].

Li et al. [7] studied the role of pore size on the specific capacitance of straw based activated carbon and tested it for supercapacitor applications in non-aqueous electrolytes. Generally, the presence of a large number of mesopores (2-50 nm) in the electrode materials provides higher capacitance values. The ACs possesses higher surface area but the limited availability of mesopores limits the specific capacitance due to lower ion accessibility [8]. Thus, the utility ratio of a high specific surface

area is also essential to the better performance of supercapacitors [9].

3.1.2 Carbon cryogels and carbon aerogels

Carbon cryogels and carbon aerogels are unique porous materials consisting of interconnected nanometer-sized particles with small interstitial pores (< 50 nm). They possess attractive properties like very high surface area (400-1100 m²/g), high electrical conductivity (25-100 S/cm), better surface chemistry and tunable porous structure which are well suited as electrodes for SCs with high energy density and long cyclic stability [10-13].

Biener et al. fabricated advanced carbon aerogels by sol gel method [14] and they exploited the electrochemical behavior of these materialstowards SC applications. Surface modified carbon cryogels fabricated by Sepehri et al. was tested towards energy storage applications and showed a specific capacitance of 120Fg⁻¹ [15].

3.1.3 Carbon nanotubes (CNTs)

Carbon nanotubes (CNT) are nanostructured cylindrical allotrope of carbonproduced by catalytic decomposition of certain hydrocarbons. CNTs are generally categorized as single-walled CNT (SWCNT) and multi-walled CNT (MWCNT) based on the

number of graphene-structured layers in each tube. Owing to their superior properties such as high conductivity like metals, good mechanical property, benign chemical and thermal stability, as well as unique porosity, they are much preferred as electrode materials for high power density devices.

The supercapacitor electrodes prepared from MWCNT were first reported by Niu et al. [16] with specific capacitance, power density and energy density of values of 113 Fg^{-1} , 8 kW kg^{-1} and 0.56 Whkg^{-1} , respectively, when 38 wt% H_2SO_4 aqueous solution was used as the electrolyte. Printable thin film SCs using single wall carbon nanotubes (SWCNT) on plastic developed by Kaempgen et al. [17] showed energy and power densities of 6 Whkg^{-1} and 70 kWkg^{-1} respectively.

3.1.4 Graphene

Graphene is a single layer of tightly-packed carbon atoms bonded in a hexagonal lattice. The specific structure exhibits high mechanical stability, high thermal stability, remarkable electrical conductivity besides providing a better platform for the storage and transportation of ions and electrons. In addition, graphene also has an extraordinary high specific surface area ($2675 \text{ m}^2/\text{g}$) which especially benefits for the performance of electric double layer capacitors. However, graphene sheets easily form irreversible agglomerates and

restack to the graphitic structure. To overcome this problem, graphene can be hybridized with CNTs, Carbon Nano Fibres (CNFs) and porous carbon.

Many graphene-based electrode materials of supercapacitors have been studied both in aqueous and organic electrolytes. Utilizing graphene materials as electrodes for supercapacitors, Wang et al. [18] reported a specific capacitance of 205 Fg^{-1} , power density of 10 kWkg^{-1} and an energy density of 29 Whkg^{-1} in an aqueous electrolyte. Kim et al. fabricated activated graphene based carbons with unique pore structure and tested their potential as supercapacitor electrode [19]. This novel material was reported to exhibit a specific capacitance of 147 Fg^{-1} with a power density of 398 kWkg^{-1} and an energy density of 74 Whkg^{-1} . In general, carbon-based materials with high surface area and suitable porous structure rather being used directly as electrode material are widely used to form composites with pseudocapacitive materials to improve the electrochemical properties of the electrode.

3.2 Metal oxides and its composites

Metal oxides attract considerable attention as smart candidates to construct high energy, high power supercapacitors because of their outstanding structural flexibility and high specific capacitance besides having a variety of oxidation states available for redox charge

transfer. The energy storage of metal oxides is predominantly based on the reversible Faradaic reaction on the surface of the oxides in addition to the normal surface storage leading to a high energy density than EDLC. Nanostructured metal oxides like ruthenium oxide (RuO_2), manganese oxide (MnO_2), nickel oxide (NiO), cobalt oxide (Co_3O_4), titanium oxide (TiO_2), iron oxide (Fe_2O_3), vanadium pentoxide (V_2O_5) and some metal hydroxides are exploited as smart candidates for supercapacitor electrode applications.

However, lower electrical conductivity and structural collapse during cycling hampered the electrochemical performance of TMOs. To overcome these problems and to produce commercial supercapacitors, two strategies may be adopted (i) to form mixed transition metal oxides, and (ii) to form carbon based (CNT, graphene) hybrid composites.

3.2.1 Ruthenium oxide (RuO_2) based electrodes

Among the transition metal oxides, ruthenium oxide (RuO_2) has been extensively studied because of its wide range of advantageous characteristics like low resistivity, metallic type conductivity, good thermal stability and long cycle life [20]. The specific capacitance of RuO_2 depends on factors including crystallinity,

particle size, and electrode architecture. For instance, it has been shown that the amorphous hydrous ruthenium oxide exhibited a much higher specific capacitance (720 Fg^{-1}) than its anhydrous counterpart [21]. RuO_2 nanotubes fabricated and tested as a supercapacitor electrode by Zhang et al. [22] reported a specific capacitance of 860 Fg^{-1} at a current density of 500 mA g^{-1} in H_2SO_4 electrolyte. Enhancement in capacitance could be achieved by a fine grained process such as annealing, deposited on high-porous current collector or fabricated into composite materials [23-25]. Although ruthenium oxides have promising electrochemical properties, its use as a supercapacitor electrode material is limited due to its high cost and environmental issues.

3.2.2 Manganese dioxide (MnO_2) based electrodes

Manganese dioxide (MnO_2) is considered as a better alternate for RuO_2 as an electrode material for supercapacitors due to its low cost, excellent capacitive performance in aqueous electrolytes and environmental benignity [26-27]. C.K. Lin [28] reported that manganese oxide electrodes, prepared via sol-gel method exhibit specific capacitance of 53.2 Fg^{-1} , 230.5 Fg^{-1} , 185.6 Fg^{-1} and 189.9 Fg^{-1} after heat treating at $250 \text{ }^\circ\text{C}$, $300 \text{ }^\circ\text{C}$, $350 \text{ }^\circ\text{C}$ and $400 \text{ }^\circ\text{C}$, respectively. Employing sonochemistry method,

Wang et al. [29] synthesized porous structured MnO_2 which was used to fabricate asymmetric capacitor with better electrochemical performance in Na_2SO_4 and KOH aqueous solutions.

3.2.3 Nickel oxide (NiO) based electrodes

The salient features like easy synthesis, low cost, higher theoretical capacitance and environmental friendliness of nickel oxide (NiO) make them to be used as a promising electrode material for supercapacitors. Using hydrothermal process and using an anionic surfactant, Purushothaman et al. have synthesized NiO microstructures [30]. The effect of temperature (120 °C, 140 °C and 160 °C) on structural and electrochemical features on NiO micro structures was studied which revealed nanostructures prepared at 160°C exhibits a highest capacitance of 989 Fg^{-1} . Better cycling stability (97% capacitance retention after 1000 charge/discharge cycles) and energy density of 49 Whkg^{-1} for this material were also reported. H.Y. Wu et al. synthesized Nickel oxide by an electrochemical strategy which produced an ultrahigh specific capacitance of 1478 Fg^{-1} in 1 M KOH aqueous solution electrolyte [31].

3.2.4 Cobalt oxide (Co_3O_4) based electrodes

Cobalt oxide is yet another transition metal oxide studied as an electrode material for supercapacitor application. Co_3O_4 has low

environmental toxicity, high theoretical capacitance and is of low cost. Yuan et al. prepared a hierarchically porous Co_3O_4 film by electrodeposition method via liquid crystalline template, and specific capacitances of 443 Fg^{-1} at 2 Ag^{-1} and 334 Fg^{-1} at 40 Ag^{-1} respectively were reported [32]. Meher et al. synthesized porous Co_3O_4 by hydrothermal method [33] which yielded a specific capacitance of 548 Fg^{-1} with cyclic stability 98.5% up to 2,000 cycles and could exhibit good Columbic efficiency.

3.2.5 Titanium dioxide (TiO_2) based electrodes

TiO_2 has been tried as an electrode material as an alternative or co-material for other metal oxides. TiO_2 is non-toxic, inexpensive and available in abundance. One-dimensional TiO_2 nanotubes have a highly accessible surface, provides a direct pathway for charge transfer and features good electrochemical behavior and chemical stability [34-35]. Hydrogenated TiO_2 nanotube arrays fabricated by Lu et al. [36] when put to electrochemical studies, exhibited an aerial capacitance of 3.24 mFcm^{-2} at a scan rate of 100 mVs^{-1} with capacitance retention of 96.9 % upto 10,000 cycles. A high specific capacitance of 1232 Fg^{-1} is realized for highly ordered TiO_2 nanotube arrays prepared by Zhou et al. [37]. The influence of porosity on electrochemical features of sol-gel processed

TiO₂ thin films was discussed by Brezesinski et al. [38].

3.2.6 Iron oxide (Fe₂O₃) based electrodes

One of the potential electrode materials for supercapacitors are iron oxides (Fe₂O₃) due to their natural abundance, suitable electrochemical performance and environmental benignity [39-40]. The amorphous Fe₂O₃ thin film prepared by Kulal et al. displayed a specific capacitance of 178 Fg⁻¹ [41]. Adopting electro spinning technique, Binitha et al. prepared α-Fe₂O₃ nanostructures and studied its morphological and electrochemical features to report a specific capacitance of 256 Fg⁻¹ with 82% of capacitance retention after 3000 cycles [42]. Combining iron oxides with carbonaceous materials (graphene or CNT) has shown enhanced capacitive properties [43]. Fe₃O₄/reduced graphene oxide nanocomposites exhibit a high specific capacitance of 480 Fg⁻¹ [44] coupled with an improved cycling performance. However, the high cost of graphene limits its wide application.

3.2.7 Vanadium pentoxide (V₂O₅) based electrodes

Among the many transition-metal oxides, vanadium pentoxide has promising potential as an electrode material for supercapacitors due to their high specific capacitance and wide potential window. V₂O₅ layered nanostructures are known to have very stable crystal structures and high faradaic

activity. However, V₂O₅ has low electronic conductivity. Integrating vanadium pentoxides with carbon-based materials is an effective strategy to enhance its poor electronic conductivity and to increase the total surface area. Lee et al. electrodeposited an ultrathin V₂O₅ layer on a self-standing carbon nanofiber paper [45] and obtained a high specific capacitance of 1308 Fg⁻¹ in a 2 M KCl electrolyte. The high capacitance of the V₂O₅ is attributed to the large external surface area of the carbon nanofibers and the maximized active sites for redox reactions of the ultrathin V₂O₅ layer. B. Saravankumar et al. [46] synthesized V₂O₅ nanoporous network via simple capping-agent-assisted precipitation technique and studied the effect of annealing temperature on the morphology, electrochemical and structural properties and stability upon oxidation–reduction cycling for supercapacitor application. The interconnected nanoporous network creates facile nanochannels for ion diffusion and facilitates the easy accessibility of ions which accounts for the high specific capacitance of 316 Fg⁻¹ as reported by the authors.

3.2.8 Mixed metal oxide based electrodes

The blending of two different metal oxides synergetically take full advantage of both kinds of metal oxides and form heterostructures which reduce the inactive sites present in the materials. Benefiting from their remarkable

electrochemical properties, the mixed metal oxide nanostructures have attracted increasing research interest towards constructing low-cost, environmentally friendly supercapacitors with enhanced electrochemical performance.

Zhonghua Ren and co-workers [47] grown $\text{Ni(OH)}_2/\text{MnO}_2$ hybrid nanosheets by self-reaction of Ni foam substrates in KMnO_4 solution at room temperature. The obtained hybrid nanosheets exhibit a high specific capacitance of $2,937 \text{ F g}^{-1}$. Rakhi et al. [48] directly grown mesoporous Co_3O_4 nanosheet arrays onto carbon paper. Utilizing electro deposition method, they additionally deposited hydrous RuO_2 nanoparticles on the obtained material. Owing to the presence of RuO_2 , the as-prepared mixed oxides system provided a specific capacitance of 905 F g^{-1} associated with an excellent rate capacity and capacity retention up to 5,000 charge discharge cycles. Yang and co-workers [49] using self-organizing anodization technique fabricated $\text{V}_2\text{O}_5\text{-TiO}_2$ nanotubes and reported a specific capacitance of 220 F g^{-1} and energy density of 20 Wh kg^{-1} with good reversibility and better stability (100% up to 600 cycles).

3.2.9 Metal hydroxide based electrodes

From the literature, it is obvious that electrodes based on metal hydroxides have been utilized to achieve enhanced electrochemical performance in SCs. For instance, mesoporous

structured $\beta\text{-Ni(OH)}_2$ directly grown on to Ni foam by Lu et al. [50] with an ultra-thin nano walls of about 6 nm showed a better cycling performance (>96% for 500 cycles) and a superior specific capacitance of 2675 F g^{-1} which is higher than the theoretical value. Employing cathodic electro deposition method and without using any surfactants, Aghazadeh et al. [51] prepared nickel hydroxide nanoparticles and analyzed its structural and morphological investigations which revealed the presence of brucite crystal phase of $\beta\text{-Ni(OH)}_2$ with particle size of 5 nm. Further, a large specific capacitance of 740 F g^{-1} was observed for this Ni(OH)_2 nanoparticles.

3.3 Hybrid electrodes

The slow ion transportation kinetics and low value of electrical conductivity of metal oxides can be improved with the help of high conductivity carbon based materials like activated carbon, carbon nanotubes (CNTs) and graphene to realize SCs with high energy and high power capabilities.

Chen et al. prepared RuO_2 nanowire/SWCNT hybrid films which exhibited a specific capacitance of 138 F g^{-1} , power density of 96 kW kg^{-1} and energy density of 19 Wh kg^{-1} [52]. Yu et al. used novel conductive wrapping approach to fabricate conductively wrapped hybrid graphene/ MnO_2 electrodes for supercapacitor electrode

applications [53]. This material exhibits a specific capacitance of 380 Fg^{-1} with cyclic stability of 95% capacitance retention upto 3,000 cycles.

3.4 Conducting polymers

Conductive polymers are pseudocapacitor materials and are generally lightweight, low-cost, non-harmful to environment and have high conductivity, unique three-dimensional (3D) porous structure, fast charge-discharge kinetics and wide potential window making them promising candidates in the development of supercapacitor electrodes. During charging and discharging process, redox reactions occur not only on the surface of the conductive materials but also in the bulk. Popular conductive polymers are polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and their derivative materials. The potential range and right electrolyte plays a key role in the performance of conductive polymer based supercapacitors. Electrolytes such as H_2SO_4 , NaOH etc. are commonly used in conducting polymer supercapacitors.

G.A. Snook et al. [54] synthesized polyaniline nanofibers which exhibited a specific capacitance as high as 601 Fg^{-1} at 1 Ag^{-1} . This performance is attributed to the hollow structure of the nanofibers. Liu et al. reported the preparation of polyaniline and polypyrrole

nanowires towards supercapacitor electrode application [55]. They achieved higher stability of 95% up to 10000 cycles with carbon coating over this conducting polymer. Polypyrrole hydrogels prepared by Shi et al. [56] through simple chemical route offered a specific capacitance of 380 Fg^{-1} due to its unique three-dimensional (3D) porous microstructure. The cycling stability of conductive polymers remains uncertain due to the mechanical stress induced by the charging-discharging process which hinder their usage as supercapacitor electrode materials.

4. NANOSTRUCTURED CuO AS ELECTRODE MATERIALS FOR SUPERCAPACITORS

Among the TMOs, copper oxide (CuO) is an important p-type transition-metal oxide with a narrow band gap ($E_g = 1.2 \text{ eV}$) and has been explored as an electrode material for high-power supercapacitors due to its characteristics like natural abundance, low cost, non-toxicity and environmental compatibility.

Simple fabrication procedure and cost effectiveness of nanostructured materials are much favoured for mass production and commercialization. Synthesizing unique CuO nanostructures could mitigate poor cyclic stability and lower conductivity because nanostructures may endow additional pathways for electrolyte penetration and maintain the

sustainability of the crystal structure during cycling.

Shaikha presented the synthesis of ruthenium (Ru) doped nanostructured copper oxide (CuO) thin films by colloidal solution method and ionic liquid [57]. Cyclic voltammetry study revealed the highest specific capacitance of 406 F g^{-1} for 15 volume percent of Ru doping concentration. This was the first successful step towards development of ecofriendly CuO based supercapacitors in task specific IL synthesized by green technology.

CuO nanosheet arrays were fabricated on nickel foam by Guiling Wang et al., using template-free growth method and its electrochemical properties were studied [58]. The results exhibit a specific capacitance of 569 F g^{-1} at a current density of 5 mA cm^{-2} in 6 M KOH electrolyte. Utilizing template-free growth method, Jichun Huang et al. [59] fabricated CuO nanosheet and doped it with Ag via the silver mirror reaction. The authors reported that the thickness of a single nanosheet was up to around 150 nm and the Ag-doped CuO nanosheet electrode could yield a specific capacitance of 689 Fg^{-1} at 1 Ag^{-1} and 299 Fg^{-1} at 10 Ag^{-1} , respectively, much higher than that of the unmodified CuO nanosheet arrays.

CuO thin films are successfully synthesized by Dubal et al. using a surfactant assisted chemical bath deposition method [60].

Electrochemical analysis confirmed a maximum specific capacitance of 411 Fg^{-1} at 5 mV s^{-1} in 1 M Na_2SO_4 for the CuO sample prepared using an organic surfactant (Triton X-100).

Yu Xin Zhang et al. [61] synthesized nanostructured CuO via facile and scaleable wet-chemical method, accompanied with calcination. For the as-synthesized CuO nanosheets, they achieved a maximum specific capacitance of 88.5 Fg^{-1} at the scan rate of 2 mV s^{-1} in 6 M KOH electrolyte. The capacitance retention of CuO nanosheets was around 90.6 % after 500 charge/discharge cycles at a current density of 5 mA cm^{-2} . The electrochemical results confirmed that the specific capacitance of the nanostructured CuO strongly depended on their morphologies (nano-sheets-like, bundle-like and flower-like CuO). Flower-like CuO nanostructures prepared by Zhang et al. [62] displayed a higher specific capacitance of 133.6 F g^{-1} in 6 M KOH electrolyte, which is about three-fold higher than commercial CuO powder.

In the study of Zhao [63] et al., a leaf-like porous CuO-graphene nanostructure synthesized by hydrothermal method delivered a specific capacitances of 331.9 and 305 Fg^{-1} at current densities of 0.6 and 2 Ag^{-1} , respectively. The authors attributed the capacity retention of 95.1% after 1000 continuous charge-discharge cycles to the improvement of electrical contact by graphene and mechanical stability by the layer-by-layer structure.

Copper oxide (CuO) nanoparticles have been synthesized by AfshinPendashteh et al. through a sonochemical assisted precipitation followed by thermal treatment [64]. They anchored the as-prepared CuO nanoparticles on the surface of graphene oxide (GO) nanosheets through a simple electrostatic co-precipitation technique. Further, the authors assembled symmetric supercapacitors in real two-electrode configurations and reported a specific capacitance of 245 Fg^{-1} at current density of 0.1 Ag^{-1} .

Girish S. Gund et al. [65] demonstrated the surfactant assisted fabrication of CuO nanostructures in thin film form directly grown onto a stainless steel substrate using a binder free hydrothermal approach. Further, they investigated the impact of organic surfactants such as Triton X-100 (TRX) and polyvinyl alcohol (PVA) on the structural, morphological, surface area and electrochemical properties of CuO nanostructures. Based on the electrochemical tests, they reported a high specific capacitance of 535 Fg^{-1} at a scan rate of 5 mV s^{-1} with 90% capacitive retention after 1000 cycles for the prepared material.

Issues like low ionic conductivity, poor electrode kinetics and cyclic stability of transition metal oxides (TMO) was addressed by Purushothaman et al. [66] by adopting the strategy of combining carbon-based materials

with TMOs. They prepared CuO/reduced graphene oxide (RGO) nanocomposite electrodes by a simple, low cost hydrothermal method which exhibited a high specific capacitance of 326 F g^{-1} at a current density of 0.5 Ag^{-1} . Further, they constructed symmetric hybrid capacitors to realize a specific capacitance of 97 F g^{-1} at 0.2 Ag^{-1} with a power density of 72 W kg^{-1} .

Moosavifard et al. [67] employed facile low-temperature solution method to synthesize one-dimensional hierarchical hybrid nanostructure composed of CuO nano rod arrays grown on carbon nanofibers. Investigating the electrochemical properties of this material produced a high capacitance of 398 Fg^{-1} at 1 Ag^{-1} in 3M KOH electrolyte. The electrochemical stability of the material for 5000 continuous cycles demonstrates the excellent cycling performance at different current densities.

CuO nanowires of diameter 30-50 nm were developed by Vidyadharan et al. using an aqueous polymeric solution based electro spinning process. The specific capacitance evaluated from the discharge curve was 620 Fg^{-1} in 6 M KOH at a current density of 2 Ag^{-1} [68]. The authors attribute the larger specific capacitance of CuO nanowires to the lower wire diameter that enhances the available surface area, high electrical conductivity owing to the one-dimensional morphology and superior crystallinity of the prepared material. Further,

they fabricated an asymmetric supercapacitor (ASC) employing CuO nanowires as anode and activated carbon (AC) as cathode. The ASC showed a specific capacitance of 83 Fg^{-1} and exhibited a superior performance than a control symmetric electrochemical double layer capacitor (EDLC).

Yang Lu reported a novel, low-cost strategy to synthesize copper oxide (CuO) nanostructures as high performance supercapacitor electrodes using an alkaline solution oxidation method [69]. The obtained electrode delivered a remarkable specific capacitance of 520 F g^{-1} at 1 A g^{-1} and a capacitance retention of more than 95% after 3500 cycles.

Copper oxide (CuO) nanoflowers on flexible copper foil (Cu) were fabricated by Shinde et al. [70] using chemical synthesis method. On evaluating the supercapacitive properties, CuO nanoflower electrode exhibit a high specific capacitance of about 498 F g^{-1} at a scan rate of 5 mV s^{-1} , with a high energy density of 26 W h kg^{-1} in 1 M KOH electrolyte besides possessing an excellent cycling stability, retaining 84% of initial capacitance after 2000 cycles.

Employing a binderless and surfactant free chemical synthesis, Nwanya et al. fabricated nanosheet-like and nanorod-like CuO films deposited on indium tin oxide (ITO) substrates

using the successive ionic layer adsorption and reaction (SILAR) approach [71]. The nanostructured CuO showed a highest specific capacitance of 566.33 Fg^{-1} at a scan rate of 5 mVs^{-1} . Stability tests utilizing GCD indicate that there is no degradation after 1000 cycles with the film yielding 100% coulombic efficiency.

Suresh et al. [72] adopted simple co-precipitation technique to synthesize CuO nanospindles and nanoworms. They reported CuO nanostructures annealed at 400°C revealed a higher specific capacitance of 345 Fg^{-1} , lower charge transfer resistance (3.3Ω) and better cycling stability. Further, they constructed asymmetric and symmetric type supercapacitor devices based on Mn doped CuO nanostructures and activated carbon as electrodes in 2 M KOH aqueous electrolyte. The Mn-CuO // 2 M KOH // AC asymmetric supercapacitor exhibited a specific capacitance of 72 Fg^{-1} along with an energy density of 7.4 Whkg^{-1} besides retaining 71 % of initial capacitance after 300 cycles [73].

Bhise et al. [74] synthesized hierarchical CuO nanosheets through a facile, eco-friendly reflux deposition approach and studied its electrochemical properties in novel 0.1 M aqueous 1-(1'-methyl-2'-oxo-propyl)-3-dimethylimidazolium chloride [MOPMIM] [Cl] ionic liquid as an electrolyte. They demonstrated that the CuO nanosheets exhibit a specific

capacitance of 180 F g^{-1} at a scan rate of 10 mV s^{-1} which is the highest value in ionic liquid electrolyte. Moreover, the sample retains 87 % of specific capacitance after 5000 cycles.

CuO/Co₃O₄ nanocomposites were prepared on Ni foam substrates via a facile hydrothermal method by Hee-Je Kim et al. [75]. The authors performed CV, GCD and EIS to evaluate the electrochemical behavior of the electrode in a three-electrode system with 3M KOH as electrolyte. The CuO/Co₃O₄ electrode exhibited a maximum specific capacitance of 806.25 Fg^{-1} at 2 Ag^{-1} and delivered a maximum energy density of $71.66 \text{ W h kg}^{-1}$ and a power density of 800 W kg^{-1} . The authors reported a cycling stability of 99.75% retention after 2000 cycles and concluded that the better performance of the composite CuO/Co₃O₄ electrode was due to the improved surface morphology with a high surface area, which facilitates electron diffusion at the electrode/electrolyte interface.

Subalakshmi et al. [76] synthesized CuO micro balls by time and cost effective hydrothermal method and studied its electrochemical performance as an active material for super capacitor application in 6 M KOH solution. They reported a specific capacitance of about 470 F g^{-1} for the CuO micro balls at a current density of 0.5 Ag^{-1} and credited the superior electrochemical performance of CuO micro balls to the 3D micro structure assembled

from nano sheets which eventually possess more active sites. Further, they concluded that the co-existence of Cu₂O phase enhances the electrochemical performance by reversible redox couple CuO/Cu₂O and the entrapped hydroxyl group in CuO micro balls increases the conductivity and accelerates the electrode kinetics in alkaline medium.

Bu et al. [77] prepared copper oxide (CuO) and CuO/reduced graphene oxide (rGO) films by using a hydrothermal method. They tested the electrochemical properties of the prepared samples films and explored the specific capacitance of CuO/rGO (80 F g^{-1}) was more than four times that of CuO (20 F g^{-1}) at a current density of 2 Ag^{-1} . They ascribed the enhanced capacitive performance to the combination of EDLC from rGO nanostructures and pseudocapacitance from CuO nanoparticles as well as to the deduced graphene restacking.

The following table summarizes the electrochemical properties of CuO based materials.

Table 1.1 Electrochemical properties of CuO based materials

S.No.	CuO based electrode	Fabrication method	Electrolyte	Specific capacitance (Fg ⁻¹)	Cyclic stability	Ref [Year]
1.	Ru doped nanostructured CuO thin films	Colloidal solution	1M [CMIM] [HSO ₄] Ionic Liquid (IL)	406	-	57[2011]
2.	CuO nanosheet arrays	Template-free growth	6 M KOH	569	83 % after 500 cycles	58 [2011]
3.	Ag doped CuO nanosheet	Template-free growth	6 M KOH	689	61% after 2000 cycles	59 [2012]
4.	CuO thin films	Chemical bath deposition	1 M Na ₂ SO ₄	411	85 % after 2000 cycles	60 [2013]
5.	Hierarchical CuO Nanostructures	Wet chemical method	6 M KOH	88.5	90.6 % after 500 cycles	61 [2013]

6.	Flower-like CuO nanostructures	Wet chemical method	6 M KOH	133.6	-	62 [2008]
7.	CuO + graphene	Hydrothermal	-	331.9	95.1 % after 1000 cycles	63 [2013]
8.	CuO/GO composite	Sonochemical	1M Na ₂ SO ₄	245	79 % after 1000 cycles	64[2013]
9.	Porous CuO nanosheet	Hydrothermal	1 M Na ₂ SO ₄	535	90 % after 1000 cycles	65 [2013]
10.	CuO/reduced graphene oxide (RGO)	Hydrothermal	0.5M K ₂ SO ₄	326 97 (Device)	100 % after 1500 cycles	66 [2014]
11.	CNF @ CuO NR	Solution method	3M KOH	398	91.9 % after 2000 cycles	67 [2014]

S.No.	CuO based electrode	Fabrication method	Electrolyte	Specific capacitance (Fg ⁻¹)	Cyclic stability	Ref [Year]
12.	CuO nanowires	Solution method	6 M KOH	620	-	68 [2015]
13.	Porous CuO nanostructures	Alkaline solution oxidation method	1 M KOH	520	> 95 % after 3500 cycles	69 [2015]
14.	3D-flower-like CuO nanostructure	Chemical Bath Deposition (CBD)	1M KOH	498	84 % after 2000 cycles	70 [2015]
15.	CuO film	Chemical synthesis	0.5 M NaSO ₄	566.33	100 % after 1000 cycles	71 [2016]
16.	CuO nanospindles	Co-precipitation	0.5M K ₂ SO ₄	345	99 % after 1500 cycles	72 [2016]
17.	Mn doped CuO nanoflakes	Co-precipitation	2M KOH	625	84 % after 2000 cycles	73 [2016]
18.	CuO nanosheets	Chemical Bath Deposition (CBD)	0.1 M 1-(1'-methyl-2'-oxo-propyl)-3- dimethylimidazolium chloride	180	87 % after 5000 cycles	74 [2017]

19.	CuO/Co ₃ O ₄	Hydrothermal	3 M KOH	806.25	99.75 % after 2000 cycles	75 [2017]
20.	CuO micro ball	Hydrothermal	6 M KOH	470	-	76 [2017]
21.	CuO + rGO	Hydrothermal	1 M Na ₂ SO ₄	80	-	77 [2017]

5. OBSERVATIONS AND RECOMMENDATIONS

Nanostructured metal oxides with attractive electrochemical properties continue to attract researchers owing to their pseudocapacitive nature and structural flexibilities. Few recommendations for future research work and the perspective directions for the development of next generation supercapacitors are discussed as follows.

- It is imperative to develop more and more novel nanostructured materials with different morphologies and sizes in order to further increase energy/power densities, improved charge-discharge rate capability and long cycle life.
- To improve the maximization ratio of active materials in electrode materials and to find a more efficient method of developing optimized electrode structures to obtain fast electron transfer rate besides taking into account the scalable fabrication and the cost of the electrode materials.
- Moreover, it is suggested that the development of new kind

of electrode materials such as metal-metal oxide nanostructures, mixed metal oxide nanostructures, double walled and triple walled hollow spheres etc. are highly promising for achieving superior electrochemical performance.

6. CONCLUSION

The pursuit for supercapacitors with superior power and energy capabilities coupled with high cycling stability to complement or compete with batteries has evinced much interest in developing advanced electrode materials. In this review, literature data and discussion regarding the electrochemical performance of various electrode materials have been presented. Table 1 exhibits a summary of the properties and characteristics of supercapacitor electrode materials based on CuO nanostructures. Carbon-based materials such as activated carbon, CNTs and graphene have been utilized to support various metal oxides or conducting polymers for making composite electrode materials. A better understanding of charge storage mechanism of nanostructured electrode materials can guide the design of high-performance supercapacitors. The field of supercapacitor research is wide open as the chance to increase the performance of

supercapacitors still exists with copious possibilities

and discoveries of new electrode materials.

7. REFERENCES

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