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Reviewing the Capacitive Properties of Cu_2O Crystal Structure and Composite

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1. ABSTRACT

There are numerous power storage devices that are used in many aspects recently. Among them, supercapacitors attract a greater attention owing to its high power density compared with the conventional capacitors. In order to address the poor energy density limitation of supercapacitors, advancement of electrode material is crucial since the supercapacitor performance relies on the electrode material predominantly. Cuprous oxide (Cu_2O) retains its position as a good electrode material for supercapacitors due to its high theoretical specific capacitance. As the major drawback of Cu_2O, it shows inherent poor conductivity and poor cycling stability. Researchers attempted several times by varying different factors of Cu_2O electrode to make Cu_2O more efficient in supercapacitor applications. This paper reviews and contrasts the electrochemical properties of Cu_2O electrode, impact of morphology of Cu_2O and Cu_2O-GN nanocomposite electrode in supercapacitors applications.

Keywords: Supercapacitors, pseudocapacitors, cuprous oxide, supercapacitor nanocomposite electrode, graphene, Cu_2O-based electrode, GN-Cu_2O nanocomposite supercapacitors.

2. INTRODUCTION

Due to the massive urbanisation and population growth over the past century, natural resources like fossil fuels have been overused to meet the world's energy needs. Consequently, renewable energy sources will become increasingly significant in the current era. To fulfil the need of energy, reusable supercapacitors and batteries as energy storage devices have increased in substantially greater focus in the last few years. Supercapacitors, also known as ultracapacitors possess many advantageous features as long cycle life (usually more than 10^4 cycles), high power and rate capability, and fast charge/ discharge rates (a few seconds to milliseconds) [1]. As the long cycle life, SCs are capable of withstanding millions of cycles. This capability is owing to their charge storage mechanism. Based on the mechanisms of energy storing, SCs can be divided into three categories as electrochemical double-layer capacitors, pseudocapacitors, and hybrid SCs. The selection of the electrode material and its fabrication is crucial when it comes to a good supercapacitor application. There are three main types of electrode materials that are used in SC technology; such as carbon nanomaterials, conducting polymers, and transition metal oxides (TMOs). Metal oxides possess excellent specific capacitance values when compared with other materials [2]. By varying and controlling their defects and structures, it is desirable for utilizing these oxides in advanced electrode materials.

3. CAPACITIVE PROPERTY VARIATION WITH THE GROWTH METHOD, CRYSTAL STRUCTURE & COMPOSITE

3.1 Cu_2O electrode material

For supercapacitors, it is mandatory to look for electrode materials, which possess high surface area, chemical stability, light weight, high thermal stability, corrosion resistance, and cost-effectiveness [3]. Hence, the attention of the most researchers are focused into nanostructured copper oxides and hydroxides as favourable electrode materials due to their high abundancy, low cost, light weight, environmental benignity, easy preparation and the high theoretical specific capacitance. Among those, cuprous oxide (Cu_2O) possesses a high theoretical specific capacitance as 2248 F g^{-1} [4]. Further, not only it possesses higher charge mobility but also depicts better and stable electrochemical properties than CuO in aqueous, alkaline medium.

3.2 Cu_2O growth using RFM sputtering technique

S. M. Pawar et al. [5] reported synthesis of porous, granular films of copper oxides via reactive radio-frequency magnetron sputtering at the room temperature and evaluated the performance for supercapacitor electrode. Using specific capacitance of Cu_2O electrode, measured with different scan rates curve, they reported that the maximum specific capacitance was 215 F/ g and the capacitance retention was 80% after 3000 cycles at 100 mV/ s. Thus, we can assume the cyclic stability is much desirable for supercapacitor applications. As of Pawar et al. cyclic voltammetry curves showed anodic and cathodic redox peaks as in Fig. 1 (a). The proportional increment of the encircled area with the scan rate indicates the idealistic capacitive behaviour. The galvanostatic charge-discharge (GCD) measurements showed in Fig. i (b), depicts

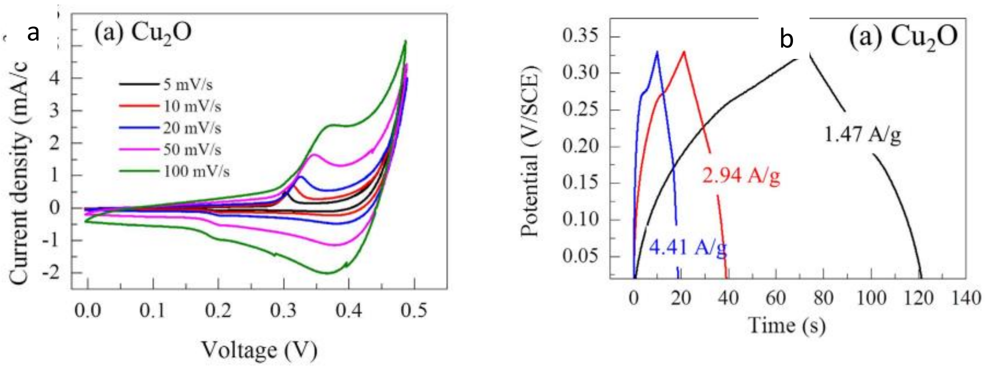

Figure 1 (a) Cyclic voltammetry curves for Cu2O at different scan rates, (b) GCD curves for Cu2O at different current densities. [5]

nearly symmetric charging discharging curves while proposing the capacitive behaviour was based on a pseudocapacitive one.

3.3 Cu_2O microspheres and microcubes

In order to synthesize Cu_2O microstructures by varying the synthesis variables and investigate their morphology dependent electrochemical supercapacitor properties was carried out by R. Kumar et al. group [6] . They used a facile hydrothermal method and varied the synthesis parameters in order to get cubic and spherical structures. When they observed the cyclic voltammetry curves of Cu_2O microspheres and microcubes, the oxidation and reduction peaks of both are shifted to positive and negative potentials respectively. They stated that this shift is responsible to an increment in the charge diffusion polarization with the redox electrode [7]. Significantly, they noticed the increase in the current response with the scan rate that implies the kinetics of interfacial Faradaic redox reactions and the fast electronic and ionic rates for high scan rates also. They obtained the specific capacitance of both microstructures by considering the area under the curve, and reported it as 645 F/g and 545 F/g respectively for Cu_2O microcubes and microspheres at 2 mV/s. Further, they were decreased with the increase of scan rate by limited diffusion and the problem of electrolyte ions migration at the electrode surface. At the lower scan rates, there was high capacitance value and it could be the bulk diffusions of electrolyte ions [8]. After 1000 cycles, the specific capacitance retention of microcubes was 55% and for microspheres, it was 42% from its initial capacitances. According to their investigation, the surface area is not differ significantly in Cu_2O microspheres and microcubes. As an important role, the energy density value was 8.6 W h/ kg for Cu_2O microspheres, and 12.8 W h/ kg for Cu_2O microcubes at 1400 W/ kg power density with 7 A/ g scan rate. Hence, the energy density is much higher in Cu_2O microcubes structure. Because of the single crystalline structure of Cu_2O microcubes, it has the better specific capacitance.

3.4 Cu_2O composites

Since Cu_2O possesses low electrical conductivity, it is hindered in use of a promising electrode material of supercapacitors although it records high theoretical specific capacitance value. Electrical conductivity plays a major role in permitting the effective ion diffusion. In such a situation, blending carbon nanomaterials with Cu_2O is highly desirable as they exhibit much more value of electrical conductivity with a high specific surface area [9]. Carbon has different forms when it comes to the usage of supercapacitor applications such as activated carbon (AC), carbon nano tubes (CNT), graphene, porous carbon, vertically aligned graphene sheets, and etc. Among these, graphene attracts as it is an excellent material in supercapacitor applications owing its high conductivity (200,000 $cm^2V^{-1}S^{-1}$), porous structure, excellent compressibility, mechanical stability, and high specific surface area than that of CNTs. Furthermore, it allows both sides to the electrolyte ions to transfer and it contributes to the EDL capacitance. Typically, EDL capacitance is lower than pseudocapacitance while showing good electrochemical cyclic stability than pseudocapacitors. Graphene is able to increase the rate of oxidation and therefore increases the pseudocapacitance. Till to date, this two-dimensional carbon material; graphene based metal/ metal oxide nanocomposites are the trendiest in research field [10].

3.4.1 Rose rock-shaped Cu_2O anchored graphene nanocomposite

Cu_2O proves to be desirable alternative as it is cheap, and abundant. W. Zhang et al. [11] reported one-pot solvothermal method, which is facile, to prepare rose rock-shaped Cu_2O anchored graphene nanocomposites (Cu_2O-GN). They discussed about the eligibility and performance of that electrode in supercapacitors well. As positive, solvothermal method is an enormously desirable synthesis method due to its cost effectiveness, and it enables fabricating nanomaterials in a convenient manner with structural variations. They reported that graphene could provide a perfect substrate to the electrochemical moieties as it contains large vacancies. On the other hand, rose rock-shaped Cu_2O enables a high accessible surface area for the effective mass transfer. According to the ring pattern of Cu_2O, the rose rock-shape was confirmed its polycrystalline nature. Furthermore, in their study, GO was their crucial material and in preparation of nanostructured- Cu_2O and its concentration can vary the nanostructures of Cu_2O.

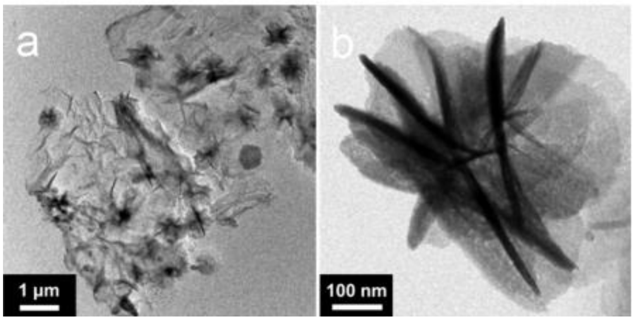

Figure 2 (a) TEM image of rose rock-shaped Gr-Cu_2O composite (b) high magnification of TEM image of Gr-Cu_2O composite [11]

In the electrochemical performance aspect, Cu_2O-GN composite was tested using 6mol L^{-1} as the electrolyte. Cyclic voltammetry curves of Cu_2O-GN composite and sole GN were depicted as in the below Fig. 3, which was reported from -1.0 V to 0.0 V vs. Hg/ HgO at a scan rate of 0.05 V/s. This proves the electric double layer capacitance of GN with a rectangular shape curve and for the Cu_2O-GN composite, rectangular shape curve with significant redox peaks was reported. These redox peaks are accountable for Cu_2O. The whole capacitance value of this nanocomposite comes as a combination of electric double layer capacitance and pseudocapacitance.

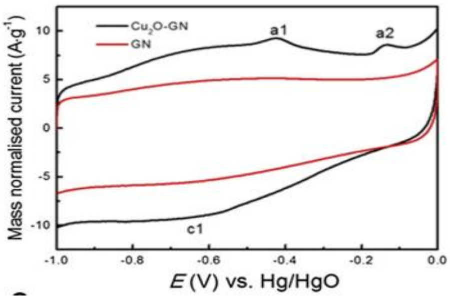

Figure 3. Cyclic voltammetry curves of the electrodes of Cu_2O-GN and GN in 6 mol L^{-1} KOH with 0.05 V s^{-1} at 25 ^{0}C [11]

When it comes to the enclosed area of the two curves, it is obvious that Cu_2O-GN composite shows a larger area than GN. This implies the higher specific capacitance of composite and recorded it as 416, 300, and 258 F/g at 1.0, 3.0 and 5.0 A/g current densities respectively. In this case the capacitance value is much higher than the solely used GN electrode since Cu_2O-GN composite furnishes more electroactive sites to the electrolyte for effective ion transfer and ultimately boosts the specific capacitance.

In graphene context, it has a possibility to aggregate while disturbing to the effective ion transfer. The formation of nanostructures of Cu_2O on GN, refrains the graphene assemble by weakening the π-π interactions and causes to fast ion transfer during the charging and discharging. Moreover, this incorporation do not allow to occur side reactions. The unique composite structure provides a high specific capacitance and facilitates a faster rate of interacting between the electrolyte and the electrodes. According to the study, this composite showed a much high value for specific energy as 42 W h/ kg and 31.8 W h/ kg at a specific power of 1500 W/ kg and 15000 W/ kg with compared to the other researches. The capacitance retention was 86% of the initial value, implying that Cu_2O-GN composite is potential candidate for the supercapacitor applications. They have examined this composite as the electrode in supercapacitor, preparing a symmetric capacitor. According to the cyclic voltammetry curve from 0.01 V/ s to 0.2 V/ s, there was a likely rectangular shape curve implying the fast charge discharge properties. Moreover, they reported 92 F/ g, and 65 F/ g specific capacitances at 1.0 A/ g and 10 A/ g current densities respectively while implying a good rate capability. When it comes to the Ragone plot, it showed 25.0 W h/ kg specific energy at 693.5 W/ kg power density and remained delivering high power as 17.7 W h/ kg energy density at 7000 W/ kg. Graphene facilitates a better substrate for the Cu_2O nanostructures and simultaneously provides electronic conductive channels while enhancing the conductivity. Not only that, graphene comes up with good interfacial contact between Cu_2O nanostructures while accelerating the electron transportation [12].

3.4.1 Graphene - Cu_2O nanocomposite/ Cu foil

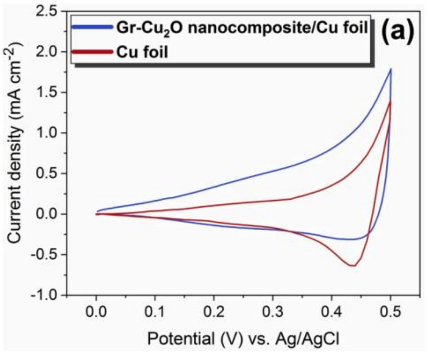

Figure 4. Cyclic voltammetry curves of Gr-Cu_2O nanocomposite/Cu foil electrode and bare Cu foil electrode at 10 mV/ s. [13]

As reported by S. Z. Golkhatmi et al. [13] group, they attempted to prepare graphene – Cu_2O (Gr - Cu_2O) nanocomposite film by incorporating graphene into the copper matrix in the electrodeposition. When the capacitive performance was evaluated of both Gr - Cu_2O nanocomposite/ Cu foil and bare Cu foil, nanocomposite exhibited a non-rectangular shape curve in cyclic voltammetry. This dominates the pseudocapacitive behaviour and it is arisen from faradaic redox reactions. The overall high capacitance value was resulted by both of the effects from electric double-layer capacitance of graphene and pseudocapacitance from Cu_2O. This was proven further with the galvanostatic charge-discharge curve study. It has shown an inconsistence of triangle shape, whilst dominating the pseudocapacitance rather than electric double layer capacitance. In the cyclic voltammetry test, when the scan rate was increased, there were no any significant change implying a good supercapacitive behaviour. At the scan rate of 10 mV/s, Gr - Cu_2O nanocomposite electrode showed a high specific capacitance value of 161.31 F/g and in high scan rates it was became lower as 108.68, 83.70, 68.00, 65.27 F/g at 30, 50, 80, and 100 mV/s scan rates, respectively.

When current response to the different voltammetric scan rates were considered (Fig. 5), cathodic and anodic currents were increased at the increment of scan rate value. The research group has concluded that the value for b was nearly equal to 0.5 in the slope and graph calculations. This indicates that the charge storage mechanism is based on the ion diffusion. The gravimetric areal capacitance of Gr-Cu_2O nanocomposite/Cu foil electrode was recorded as 44.28 mF/ cm while bare Cu foils showed 23.02 mF/ cm. When it comes to the cyclic stability of this electrode, it retained 92.48% capacitance retention after 500 cycles. This indicates its exceptional reversibility property in charging-discharging process. In order to evaluate the ragone plot according to this composite electrode, it showed 5.60 W h/ kg at 323.40 W/ kg amidst bare Cu foil showing 1.23 W h/ kg. As the next researching step, they have tested this utilizing as an electrode of an asymmetric supercapacitor. Under the cyclic voltammetry test, the supercapacitor exhibited some redox peaks in the curve, indicating redox reactions in capacitive mechanism and it has not changed the shape dramatically when increasing the scan rate from 10 to 50 mV/ s. The specific capacitance value of the cell was reported as 11.94 F/g at 10 mV/ s.

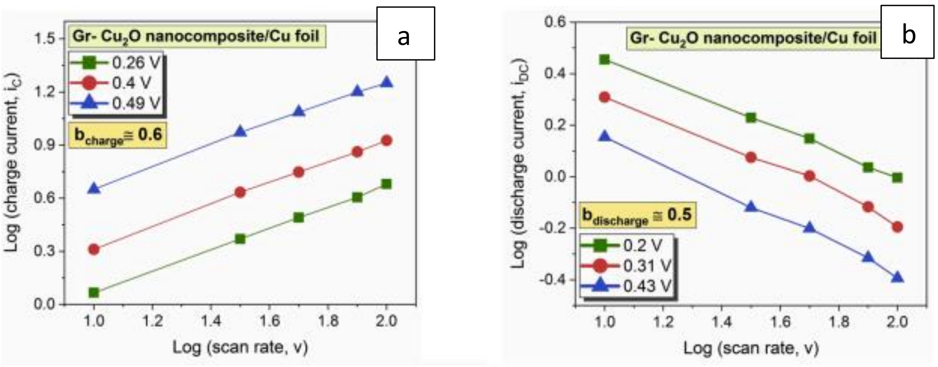

Figure 5. Linear relationship of log i vs. log ν for a) anodic (charge) and b) cathodic (discharge) sweeps of cyclic voltammetry [13]

4. DISCUSSION

Table 1 - Comparison of the specific capacitance of Cu_2O based materials in the literature

Electrode material	Synthesis method	Specific capacitance	Capacitance retention
Cu_2O granular film	Reactive radio-frequency magnetron sputtering	215 F/g at 1.47 A/g	80% after 3000 cycles
Cu_2O microcubes	Hydrothermal	660 F/g at 1 A/g	80% after 1000 cycles
Cu_2O microspheres	Hydrothermal	516 F/g at 1 A/g	-
Rose rock-shaped Cu_2O-GN composite	One-step solvothermal	416 F/g at 1 A/g	86% after 180 cycles
Gr-Cu_2O nanocomposite/Cu foil	Hydrothermal	161.31 F/g at 10 mV/s	92.48% after 500 cycles

When it comes to the supercapacitor performance, the concentration of the electrolyte is also crucial. It contributes directly to the specific capacitance value by allowing more or less ion transfer. Hence, it is preferred 6M KOH as the promising electrolyte for a better performance of a supercapacitor electrode [5]. The above results show the morphological modification of Cu_2O, has impacted more upon the specific capacitance value rather than that of the composites. As Cu_2O microcubes possess a single crystalline nature, it allows to shorter ion diffusion paths and then for ion transfer. Then the capacitance value will be higher. Although the conductivity and surface area values are higher after incorporating graphene to the Cu_2O, the capacitance value was not much higher.

5. CONCLUSION

Supercapacitors are now becoming an interesting energy storing device, enabling long cycle life, reliability and high power densities. The electrode material is crucial when it comes to its performance. In this review, we reported electrochemical performance data of `the Cu_2O electrode, different morphology structures of Cu_2O, and Cu_2O composites. In summary, electrochemical performance vastly relies on the morphology of the electrode material. Herein we have discussed further about Cu_2O-GN nanocomposite incorporation in those applications and the impact to the capacitive behaviour. The Cu_2O-GN combination facilitates well-performance in many aspects. Cu_2O can be used to prevent aggregating GN resulting expose more active sites and enhance the conductivity and effective surface area can be achieved with the incorporation of graphene into Cu_2O. It was obvious that the synergistic effect of both Cu_2O, and GN affected to the enhancement in overall capacitance. Hence, we can assume the microcube structure would be very promising electrode materials for supercapacitor applications.

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