1.1 Introduction

Climate change and the limited availability of fossil fuels have greatly affected the world economy and ecology. With a fast-growing market for portable electronic devices and the development of hybrid electric vehicles, there has been an ever increasing and urgent demand for environmentally friendly high-power energy resources. Supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted much attention because of their pulse power supply, long cycle life, simple principle, and high dynamic of charge propagation [1-2]. As illustrated in Fig. 1.1, where various energy conversion and storage devices are compared and presented in the simplified ‘Ragone plot’, supercapacitors occupy an important position in terms of the specific energy as well as the specific power. With a high power capability and relatively large energy density compared to conventional capacitors, supercapacitors offer a promising approach to meet the increasing power demands of energy storage systems in the twenty first century. Currently, supercapacitors are widely used in consumer electronics, memory back-up systems and industrial power and energy management [3]. A more recent application is the use of supercapacitors in emergency doors on the Airbus A380, highlighting their safe and reliable performance. One of the most promising applications is their use in low-emission hybrid electric vehicles, and fuel cell vehicles. In such cases, supercapacitors are coupled with primary high-energy batteries or fuel cells to serve as a temporary energy storage device with a high-power capability to store energies when braking. Supercapacitors are likely to show an equal importance to batteries for future energy storage systems [4-7].
1.2 Historical background

The storage of electrical charge in the interface between a metal and an electrolytic solution has been studied by chemists since the nineteenth century, but the practical use of double-layer capacitors only began in 1957, when a patent was placed by General Electric for an electrolytic capacitor using porous carbon electrodes [8] (Fig. 1.2). Although the patent admits that “it is not positively known exactly what takes place when the devices… are used as energy storing devices,” it was believed that energy was being stored in the pores of the carbon, and it was noted that the capacitor exhibited an “exceptionally high capacitance.” Later, in 1966, The Standard Oil Company, Cleveland, Ohio (SOHIO) patented a device that stored energy in the double layer interface [9]. At this time SOHIO acknowledged that “the ‘double-layer’ at the interface behaves like a capacitor of relatively high specific capacity.” SOHIO went on to patent a disc-shaped capacitor in 1970 utilising a carbon paste soaked in an electrolyte [10]. By 1971, however, a subsequent lack of sales led SOHIO to abandon further development and license the technology to NEC [11]. NEC went on to produce the first commercially successful double-layer capacitors under the name “supercapacitor.” These low voltage
devices had a high internal resistance and were thus primarily designed for memory backup applications, finding their way into various consumer appliances. By the 1980’s a number of companies were producing electrochemical capacitors. Matsushita Electric Industrial Co., (otherwise known as Panasonic in the Western world), had developed the “Gold capacitor” since 1978. Like those produced by NEC, these devices were also intended for use in memory backup applications [12]. By 1987 ELNA had begun producing their own double-layer capacitor under the name “Dynacap” [13]. The first high-power double-layer capacitors were developed by PRI. The “PRI Ultracapacitor,” developed from 1982, incorporated metal-oxide electrodes and was designed for military applications such as laser weaponry and missile guidance systems [14]. News of these devices triggered a study by the United States Department of Energy (DoE) in the context of hybrid electric vehicles, and by 1992 the DoE Ultracapacitor Development Program was underway at Maxwell Laboratories [15].

![The capacitor patented by General Electric](image)

**Fig.1.2** The capacitor patented by General Electric

### 1.3 Current trends of research in supercapacitors

Research is currently being conducted at a number of institutions in the interests of improving both the energy and power densities of Electric double layer capacitor technology. Activated carbon is the most commonly used electrode material in commercial supercapacitors at present, and a good deal of research is focused in determining the factors that contribute to the specific
capacitance and series resistance in such materials. A number of new materials based on carbon are being developed for improving the performance of supercapacitor electrodes. For example Carbon nanotubes (CNT) have been explored recently because of higher specific capacitance than that achievable by activated carbons [16-17]. Considerable interest has also been shown in conducting polymer materials, and research suggests that high specific capacitances could be attained using conducting polymer based composites [18]. Metal-oxides have always been an attractive electrode material due to their low resistance and high specific capacitance, but their excessive cost has generally ruled them out as a commercially viable option. Thus hybrid configurations of carbon with metal oxide or with conducting polymer could be a better option. Also of interest is the study of solid-state supercapacitors in which solid polymer electrolyte is used instead of a liquid electrolyte [19]. Solid polymer electrolytes are advantageous over liquid electrolytes as it overcomes the problem of electrolyte leakage, flexibility and ease of handling. Research is being done to develop electrochemical capacitors using ionic liquid electrolytes. These electrolytes are attractive for several reasons. First, they can be thermally stable for temperatures as high as 300°C with near zero vapor pressure and are non-flammable with very low toxicity. Further the useable electrochemical window is large leading to cell voltages as high as 4V with some carbons [20].

1.4 Future scope
Activated carbons currently dominate the market as an electrode material, but progress in the development of conducting polymers and metal oxides is continuing at a steady rate. The exploitation of pseudocapacitive effects of new materials to enhance double-layer capacitance seems to be a prevalent goal amongst current researchers, and offers a good chance of developing the next generation of high power, high-energy supercapacitors.

1.5 Basic Principle
Supercapacitors can be considered as energy storage device based on an understanding of the physical processes that take place at the electrode electrolyte interface. Electrochemical capacitors operate on principles similar
to those of conventional electrostatic capacitors except that an electrolyte is always present to form a double layer. A conventional capacitor store energy in the form of electrical charge and a typical device consists of two conducting materials separated by a dielectric and is shown in fig 1.3.

![Diagram of a conventional electrostatic capacitor](image)

**Fig. 1.3 Conventional Electrostatic Capacitor.**

When an electric potential is applied across the conductors electrons begin to flow and charge accumulates on each conductor. When the potential is removed the conducting plates remain charged until they are brought into contact again, in which case the energy is discharged. The amount of charge that can be stored in relation to the strength of the applied potential is known as the capacitance, and is a measure of a capacitor’s energy storage capability. These processes can be indicated by the following relations between capacitance and other relevant parameters.

\[
C = \frac{Q}{V} = \varepsilon A / d \quad \text{..................................................}(1.1)
\]

\[
U = CV^2 / 2 \quad \text{..................................................}(1.2)
\]

C is capacitance in Farads, Q charge in Coulombs; V is electric potential in Volts, \( \varepsilon \) is the dielectric constant of the dielectric, A is conductor surface area, d is dielectric thickness, and U is the potential energy.
1.6 Supercapacitors

Generally, on the basis of the energy storage mechanism, supercapacitors can be classified into two categories. One is the electrical double layer capacitor (EDLC), where the capacitance comes from the pure electrostatic charge accumulated at the electrode/electrolyte interface; therefore it is strongly dependent on the surface area of the electrode materials that is accessible to the electrolyte ions. The other category is the pseudo-capacitor, in which fast and reversible faradic processes take place due to electro-active species. These two mechanisms can function simultaneously depending on the nature of the electrode materials. Progress towards supercapacitor technologies can benefit from the continuous development of nanostructured materials. The Fig. 1.4 shows the taxonomy of the supercapacitor.

![Taxonomy of the supercapacitor](image)

**Fig.1.4 Taxonomy of the supercapacitor**

1.6.1 The energy storage mechanism of EDLCs.

Conventional capacitors store little by way of energy, due to the limited charge storage areas and geometric constrains of the separation distance between the two charged plates. However, supercapacitors based on the EDL
mechanism can store much more energy because of the large interfacial area and the atomic range of charge separation distances. As schematically illustrated in Fig. 1.5 a, the concept of the EDL was first described and modeled by von Helmholtz in the 19th century, when he investigated the distribution of opposite charges at the interface of colloidal particles [21]. The Helmholtz double layer model states that two layers of opposite charge form at the electrode/electrolyte interface and are separated by an atomic distance. The model is similar to that of two-plate conventional capacitors. This simple Helmholtz EDL model was further modified by Gouy and Chapman [22-23] on consideration of a continuous distribution of electrolyte ions (both cations and anions) in the electrolyte solution, driven by thermal motion, which is referred to as the diffuse layer.

![Fig. 1.5 Models of the electrical double layer at a positively charged surface: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP).](image)

The IHP refers to the distance of closest approach of specifically adsorbed ions (generally anions) and OHP refers to that of the non-specifically adsorbed ions. The OHP is also the plane where the diffuse layer begins. \(d\) is the double layer distance described by the Helmholtz model. \(\Psi_0\) and \(\Psi\) are the potentials at the electrode surface and the electrode/electrolyte interface, respectively (see Fig. 1.5b). However, the Gouy–Chapman model
leads to an overestimation of the EDL capacitance. The capacitance of two separated arrays of charges increases inversely with their separation distance, hence a very large capacitance value would arise in the case of point charge ions close to the electrode surface. Later, Stern [24] combined the Helmholtz model with the Gouy–Chapman model to explicitly recognize two regions of ion distribution—the inner region called the compact layer or Stern layer and the diffuse layer (see Fig. 1.5c). In the compact layer, ions (very often hydrated) are strongly adsorbed by the electrode, thus the name of compact layer. In addition, the compact layer consists of specifically adsorbed ions (in most cases they are anions irrespective of the charge nature of the electrode) and non-specifically adsorbed counter ions. The inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) are used to distinguish the two types of adsorbed ions. The diffuse layer region is as what the Gouy–Chapman model defines. The capacitance in the EDL ($C_{dl}$) can be treated as a combination of the capacitances from two regions, the Stern type of compact double layer capacitance ($C_{H}$) and the diffusion region capacitance ($C_{diff}$). Thus, $C_{dl}$ can be expressed by the equation (1.3).

$$\frac{1}{C_{dl}} = \frac{1}{C_{H}} + \frac{1}{C_{diff}} \quad (1.3)$$

The factors that determine the EDL behavior at a planar electrode surface include the electrical field across the electrode, the types of electrolyte ions, the solvent in which the electrolyte ions are dissolved, and the chemical affinity between the adsorbed ions and the electrode surface. As the electrode is usually a porous material with a high specific surface area, the EDL behavior at the pore surface of the porous electrode is more complex than that at an infinite planar one as the ion transportation in a confined system can be drastically affected by a number of parameters, such as the tortuous mass transfer path, the space constrain inside the pores, the ohmic resistance associated with the electrolyte, and the wetting behavior of the pore surface by the electrolyte. Fig. 1.6 schematically illustrates an EDLC made of porous carbon electrode. The capacitance estimation for an EDL-type supercapacitor is generally assumed to follow that of a parallel-plate capacitor:
\[
C = \frac{\varepsilon_r \varepsilon_0}{d} A \tag{1.4}
\]

Where, \( \varepsilon_r \) is the electrolyte dielectric constant, \( \varepsilon_0 \) is the permittivity of a vacuum, \( A \) is the specific surface area of the electrode accessible to the electrolyte ions, and \( d \) is the effective thickness of the EDL (the Debye length). Based on equation (1.4), there should be a linear relationship between specific capacitance \( (C) \) and specific surface area \( (A) \). However, some experimental results have shown that this simple linear relationship does not hold [25-26]. Traditionally it was believed that the submicropores of an electrode do not participate in the formation of EDL due to the inaccessibility of the submicropore surfaces to the large solvated ions. However, Raymundo-Pinero and co-workers [27] recently observed the important contributions of microspores to the overall capacitance and suggested that partial desolvation of hydrated ions occurred, leading to an enhanced capacitance. Very recently, Simon and Gogotsi reported an anomalous capacitance increase in carbon electrodes with pore sizes less than 1 nm. The authors observed the maximum EDL capacitance when the electrode pore size was very close to the ion size. These results further confirmed a capacitance contribution from pores with sizes smaller than the solvated ion size. Recently, Huang and co-workers [28] have reported a heuristic approach to describing nanoporous carbon-based supercapacitors. In their approach, the pore curvature is taken into account and a different capacitive behavior was proposed depending on the size of the pore. An electric double-cylinder capacitor (EDCC) model is used for describing mesoporous carbon electrodes, while an electric wire-in-cylinder capacitor (EWCC) model is proposed for modeling microporous carbon electrodes, as illustrated in Fig. 1.6. When the pores are large enough so that the pore curvature is no longer significant, the EDCC model can be reduced naturally to the traditional planar EDL model given in equation (1.4). The capacitance estimation for the two proposed models are given in equation (1.5) for the EDCC model and equation (1.6) for the EWCC model, respectively:

\[
C = \frac{\varepsilon_r \varepsilon_0}{b \ln \left[ \frac{b}{(b - d)} \right]} A \tag{1.5}
\]
in which $b$ is the pore radius, $d$ is the distance of approaching ions to the surface of the carbon electrode, and $a_0$ is the effective size of the counter ions (that is, the extent of electron density around the ions)

\[
C = \frac{\varepsilon_r\varepsilon_0}{b \ln \left( \frac{b}{a_0} \right)} A \quad \text{........(1.6)}
\]

Fig. 1.6 Schematic representation of an EDLC based on porous electrode materials.
1.6.2 Pseudocapacitance

Pseudocapacitance arises from reversible Faradaic reactions occurring at the electrode, and is denoted as ‘pseudo’-capacitance in order to differentiate it from electrostatic capacitance. The charge transfer that takes places in these reactions is voltage dependent, so a capacitive phenomenon occurs. There are two types of reactions that can involve a charge transfer that is voltage dependent.

I Redox reactions

In a redox reaction involving an oxidant, ox, and reductant, red, of the form, $ox + Ze^- \rightleftharpoons red$, the potential, $E$, is given by the Nernst equation as shown in Equation (1.7).

$$E = E^0 + \frac{RT}{zF} \ln \frac{R}{1-R}$$

$E^0$ is the standard potential, $R$ is the gas constant, $T$ is the absolute temperature, $F$ is the Faraday constant, and $R$ is defined as $[ox] / ([ox]+[red])$, (where square brackets denote species concentrations). The amount of charge $q$ (given by the product $zF$), is therefore a function of the potential $E$. Differentiation of Equation 1.6 thus produces a pseudocapacitive relation [29].

Redox pseudocapacitance in ruthenium-oxides was studied at the University of Ottawa, Canada. In Fig.1.7 the voltage/current characteristic demonstrates the highly reversible nature of the Faradic redox reactions. The charge/discharge curve is a result of overlapping redox reactions, as well as a significant double-layer capacitance due to the porous structure of the hydrous oxide [29].
Fig. 1.7 Cyclic voltammogram of a ruthenium-oxide electrode in sulfuric acid electrolyte.

**II Adsorption of ions**

The deposition of ions to form a monolayer on the electrode substrate is a reversible process that results in a Faradic charge transfer, and hence gives rise to pseudocapacitance in a similar manner to that demonstrated in redox reactions. The adsorption/desorption process can be written as Equation 1.8,

\[ A^+ + S \pm e^e \leftrightarrow S_{\text{ads}} \]

Where \( A \) is the ionic species, \( S \) is the substrate, \( c \) is the concentration of depositable ions, and \( 1 - \theta_A \) is the fractional free surface area available for adsorption at coverage, \( \theta_A \), and \( V \) is the electrode potential [30]. If it assumed that sites are occupied randomly in a fixed lattice, an equation for coverage can be determined from the Langmuir adsorption equation. This yields the relation shown in Equation 1.9.
\[
\frac{\theta}{1-\theta_A} = K e^{\frac{-VF}{RT}} \tag{1.9}
\]

\(K\) is the electrochemical equilibrium constant. A change in coverage \(dq\) is directly proportional to the charge \(q_1\), expressed by Equation 1.10.

\[
dq = q_1 d\theta \tag{1.10}
\]

where \(q_1\) is the amount of charge required to form or disperse a complete monolayer. Since \(\theta\) is a function of \(V\), differentiation of Equation 1.9 results in a pseudocapacitive relation described by Equation 1.11 [29].

\[
C_\phi = \frac{q_1 F}{RT} \frac{KC \pm e^{\frac{-VF}{RT}}}{\left(1 + K e^{\frac{-VF}{RT}}\right)^2} \tag{1.11}
\]

1.7 Capacitor construction

A wide variety of EDLC materials and processes for cell construction currently exist. This part covers the properties of various available materials and describes the aspects of each alternative that have a significant impact on device performance.

1.7.1 Electrode materials

Selection of electrode materials plays a crucial role in determining the electrical properties of a supercapacitor. Double-layer charge storage is a surface process, and the surface characteristics of the electrode greatly influence the capacitance of the cell. Carbon is the most widely used electrode material, but considerable research is being conducted into metal-oxides and conducting polymers.

1.7.2 Carbon

Carbon has been utilized as a high surface area electrode material ever since development of the electrochemical capacitor began. Today, it is still an attractive option because of its low cost, availability, and long history of use. Carbon electrodes can take a number of manufactured forms such as foams, fibers, and nanotubes.
One might expect the specific capacitance to be directly proportional to the carbon electrode's surface area; however this is not always the case. Often, a type of carbon with a lower surface area will have a higher specific capacitance than a type with a larger surface area. This is because the actual double-layer capacitance varies depending on the process used to prepare the carbon. Treatment of activated carbon materials influences the porous structure of the electrode surface, and it is the accessibility of the pores to the electrolyte that is important. The mobility of the ions within the pores is different to the mobility of ions in the bulk of the electrolytic solution, and is greatly influenced by pore size. If the pores are too small to allow easy access to electrolyte ions they will not contribute to double-layer capacitance. The pore size must therefore be chosen to suit the electrolyte and thereby ensure that the pore size distribution is optimal based upon the size of the ions [31]. The conductivity of the electrode is of great concern to the power density of an EDLC. Conductivity is inversely proportional to particle size, so a material of higher surface area and is therefore made of smaller particles develops an increased resistance. Power density is thus improved with the use of activated carbons with more large pores, though this will limit energy storage due to reduced surface area. The use of binding material also affects conductivity, and power performance is improved with a decreased percentage of binder [31]. Pseudocapacitive effects are often found to occur on the surface of activated carbons. The level of pseudocapacitance can be enhanced by treatment of the carbon to increase surface functionality. As an example, Frackowiak [31] sites the work of Miller in which the capacitance of activated carbon was enhanced by treatment with ruthenium oxides. Besides activated carbons, electrodes can also be formed from carbon aerogels. Aerogels are a suspension of carbon nanoparticles within a gel, and have a high surface-area, good conductivity, and may be used without binding material. Particle size is controlled by the preparation process, and smaller particles result in a larger accessible pore surface-area [31]. Nanotubes offer a new possibility for carbon electrodes, but are still being researched. Preliminary results suggest that higher capacitance is achieved by tangled networks with an open central canal [31].
1.7.3 Conducting polymers

Conducting polymer store and release charge through redox processes. When oxidation occurs, (also referred to as ‘doping’), ions are transferred to the polymer backbone. When reduction occurs (‘dedoping’) the ions are released back into the solution. Charging in conducting polymer films therefore takes place throughout the bulk volume of the film, and not just on the surface as is the case with carbon. This offers the opportunity of achieving high levels of specific capacitance. Work at the Los Alamos National Laboratory [32] has reported prototype polymer film capacitors with an energy density of 39 Wh/kg and a power density of 35 kW/kg.

1.7.4 Metal-oxides

Metal-oxides present an attractive alternative as an electrode material because of high specific capacitance and low resistance, possibly making it easier to construct high-energy, high-power EDLCs. Extensive research into ruthenium oxides has been conducted for military applications, where cost is presumably less of an issue than it is for commercial ventures. The US Army Research Lab has assembled prototype cells with an energy density of 8.5 Wh/kg and a power density of 6 kW/kg [33]. Academic institutions have focused on searching for other, cheaper, materials to use instead of ruthenium-oxides, but the selection has traditionally been limited by the use of concentrated sulfuric acid as an electrolyte. It was believed high capacitance and fast charging was largely a result of H sorption, so a strong acid was therefore necessary to provide good proton conductivity. This resulted in a narrow range of possible electrode materials, however, since most metal-oxides break down quickly in acidic solutions. Milder aqueous solutions such as potassium chloride have therefore been considered for use with metal-oxides such as manganese-oxides. Although manganese oxide electrodes currently appear to possess lower specific capacitances than ruthenium-oxides, the lower cost and milder electrolyte may be enough of an advantage to make them variable alternative Metal-oxide electrodes can only be used
with aqueous electrolytes, thereby limiting the achievable cell voltage. Gains in power density from lower resistance are therefore often offset by losses due to the lower operating voltage.

1.7.5 Hybrid and composites

Hybrid electrode configurations show considerable potential, consisting of two different electrodes made of different materials. Composite electrodes consist of one type of material incorporated into another within the same electrode. In the course of research into polymer electrodes at the University of Bologna it was found that a sufficiently high polymer concentration could not be realized in the negative electrode. The positive polymer electrode was successfully constructed, however, and an activated carbon was used as the negative electrode. Also of interest are the results of experiments into depositing polymers onto carbon substrates to form composite electrodes. Carbon nanotubes coated with conducting polymers have yielded particularly good results, with high specific capacitances of 180 F/g being reported [20, 21]. The improved levels of energy storage are a result of the charging taking place largely throughout the bulk of the material, along the surface of the nanotubes and along the backbone of the polymer. The pseudocapacitance arising from the redox processes in the polymer further enhances the capacitive gains.

1.7.6 Nanostructured materials

Nanostructured materials in this context have triggered great excitement, due to both fundamental interest as well as potential technological applications especially in energy research [35-37]. Size reduction in nanocrystals leads to a variety of exciting phenomena due to enhanced surface-to-volume ratio and reduced scale of transport lengths for both mass and charge transport. The benefit of narrowly spaced interfaces also results in rapid energy storage due to the reduction of the effective diffusion path. Thus, in the context of storage behavior, nanocrystalline electrodes exhibit high capacity as well as Columbic efficiency and high rate performance. Controlling the precise size and distribution of pores in novel electroactive materials may be an avenue for nanotechnology of supercapacitors to achieve more storage
performance. However, care needs to be taken to attain a compromise between specific surface area of the electrodes for high capacitance and pore-size distribution for easy access of the electrolyte [38]. One-dimensional (1D) nanostructured materials have been intensively investigated as building components in electrochemical energy storage device because they provide short diffusion path lengths to ions leading to high charge/discharge rate. 1D nanostructures may exhibit excellent electrical, electrochemical, and mechanical properties for electrochemical energy storage [39].

1.7.7 Transparent and flexible supercapacitor

There has been great interest recently in both flexible and transparent electronics such as transparent and flexible active matrix organic light-emitting diode display which may find applications in heads-up display, automobile wind-shield display, and conformable products [40]. However, to realize fully transparent and/or flexible devices, one may also consider making transparent and/or flexible energy conversion and storage units with high energy storage and power density. Supercapacitor with properties of high energy storage, small size, and lightweight has become one of the best candidates of energy storage devices [41-43]. Although some supercapacitors built on carbon nanotubes have been reported, the performance of these supercapacitors is usually not as good as redox supercapacitors made of metal oxide materials (e.g., RuO$_2$, MnO$_2$, and IrO$_2$). On the other hand, these supercapacitors are usually neither transparent nor flexible, which greatly limit their real applications in flexible or transparent electronics. It is still of great interest to develop transparent and flexible supercapacitors [44]. The transparent electrode can be obtained by (i) fabricating the nano material (ii) doping the metal and non-metal in the semiconductor.

(a) Quantum size effect:

The transparent electrode can be obtained by fabricating the nanomaterials of the semiconductors. For a semiconductor crystal, electronic excitation consists of a loosely bounded electron-hole pair (the Mott-Wannier exciton'), usually delocalized over a length much longer than the lattice constant. As the diameter of the semiconductor crystallite approaches this
exciton Bohr diameter, its electronic properties start to change. This quantum size effect can be explained qualitatively by considering a particle-in-a-box like situation where the energy separation between the levels increases as the dimensions of the box are reduced. Thus, one observes an increase in the band gap of the semiconductor with a decrease in the particle size.

On a more quantitative footing, various different theoretical approaches have been employed to account for the variation in the electronic structure of nanocrystallites as a function of its size (fig. 1.8). The first explanation for the size dependence of electronic properties in nanocrystals was given by Efros and Efros [46]. It is based on the effective masses of the electron \( m_e^* \) and the hole \( m_h^* \). Known as the effective mass approximation ~EMA!, it is solved by taking various choices for the electron and hole wave functions and solving the effective mass equation variationally. In most EMA calculations, the confining potentials for the electron and the hole have been assumed infinite. Therefore, the electron and the hole wave functions vanish at and beyond the surface of the nanocrystal, without the possibility of any tunneling. In the strong confinement regime, where \( R \), the nanocrystals radius, is much smaller than \( a_B \), the Bohr exciton radius, Brus proposed [47] the following expression for the band gap of the finite-sized system:

\[
E(R) = E_g + \frac{\hbar}{2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) \left( \frac{\pi^2}{R^2} \right) - 1.786 \frac{e^2}{\varepsilon R} - 0.248 \varepsilon R \eta \]

where, \( E_g \) is the bulk band gap. The second term is the kinetic-energy term containing the effective masses, \( m_e^* \) and \( m_h^* \), of the electron and the hole, respectively. The third term arises due to the Coulomb attraction between the electron and the hole, and the fourth term due to the spatial correlation between the electron and the hole which is generally small compared to the other two terms.
Variation in the electronic structure of nanocrystallites as a function of its size

(b) Metal and nonmetal doping in metal oxides:

Electronic structures of Oxides:

The electronic structures of oxides are largely different from those of covalent semiconductors and are shown in Fig. 1.9 (a). For, example, for Si, conduction band minimum (CBM) and valence band maximum (VBM) are made of anti-bonding (sp$^3$ $\sigma^*$) and bonding states (sp$^3$$\sigma$) of Si sp$^3$ hybridized orbitals and its band gap is formed by the energy splitting of the $\sigma^*$-$\sigma$ levels.

In contrast, as oxides have strong ionicity, CBM and VBM are usually formed by different ionic species. The most important factor to
understand electronic structures in ionic crystals is the Madelung potential. When metal atoms and oxygen atoms come close, charge transfer occurs due to large difference in electron affinity and ionization potential, which ionizes these atoms. The ions form negative electrostatic potential at the cationic sites and positive potential at the anionic sites (Madelung potential), which consequently stabilizes the ionized states in the crystal structure. Therefore the CBMs are mainly made of the metal cation and VBMs of oxygen 2p orbital in typical oxides. Main group oxides have large bandages because the large Madelung potential increases the energy splitting.

For transparent conductive oxides (TCOs), CBMs are mainly made of s orbitals with a large principle quantum number n. These s orbitals have large spatial size and form large hybridization even with second neighbor metal cations. This is the reason why TCOs have small electron effective masses. Such oxides can be good electrical conductors as long as high carrier doping is possible.

In contrast to n-type TOSs, it is much difficult to attain good p-type conduction in TOSs because hole transport paths in typical oxides are mainly made of O2p orbitals (Fig.1.10 (a)), but they are rather localized. Therefore, hole effective masses are rather large and VBM levels are deep. The former results in small hole mobilities and the later causes difficulty in hole doping. These are reasons why only n-type oxides were known for TCOs before 1997 [48].

A way to attain p-type conduction is to increase the dispersion of VBM, which would be achieved by (i) decreasing the nearest neighboring oxygen-oxygen distance, (ii) using the hybridization of metal orbitals whose energy levels are close to those of O2p or (iii) employing more extended orbitals for anions. Exceptionally, in Cu2O, the top of the valence band states is derived from fully occupied Cu 3d states close to the O 2p states and is more mobile when converted into holes. Interestingly, p-type transparent conductive oxides based on Cu2O such as CuAlO2, CuGaO2 and SrCu2O2 have modified energy band structures to reduce oxygen mediated d-d coupling between the Cu atoms, resulting in the enlargement of their optical band gaps [49-51]. Conversely, the top of the valence band of Cu2O can be narrowed by reducing Cu d-d interactions, widening the band gap. Furthermore, from another
standpoint of band gap engineering, the introduction of N as a dopant into substitutional O sites in TiO$_2$ was effective for optical band gap modulation of TiO$_2$-based photocatalysts. Subsequently, several methods of doping in which nonmetal atoms such as N, S, and C are introduced into the TiO$_2$ lattice have been reported to shift the absorption edge. Yoshitaka Nakano report on the effect of N doping into Cu$_2$O films prepared by reactive magnetron sputtering in view of optical band gap engineering by substitutionally incorporated into the O lattice sites and is shown in Fig.1.10 (b) [52].

![Diagram of electronic structures](image)

Fig.1.9 Electronic structures of (a) covalent and (b) ionic semiconductor.
Fig. 1.10  The effect of doping on electronic structure of transparent conducting oxides
1.8 Copper Oxide

Copper oxides exist in two stable forms, the cuprous oxides \( \text{Cu}_2\text{O} \) and the cupric oxides \( \text{CuO} \). These two oxides have very different colors, crystal structures, and physical properties. Simple chemistry tells that these differences are mainly due to the fact that Cu in \( \text{Cu}_2\text{O} \) is in the \( \text{Cu}^+ \) state. \( \text{Cu}_2\text{O} \) is a red-colored cubic semiconductor that displays a wealth of interesting excitonic levels. \( \text{CuO} \) on the other hand has a dark, iron gray color and crystallizes in a more complicated monoclinic tenorite structure exhibiting interesting antiferromagnetic ordering. \( \text{CuO} \) has also known as p-type semiconductor that exhibits a narrow band gap (1.2 eV) [53]. Due to the appearance of high Tc superconductors of \( \text{CuO} \) materials, it has received much attention science 1986. Their superconductivities are controlled by the structure, composition and the type and density of carriers. It also exhibits other interesting properties. For example, monoclinic \( \text{CuO} \) solid belongs to a particular class of materials known as Mott insulators, whose electronic structures cannot be simply described using conventional band theory. Recent studies by several groups indicate that it could exist in as many as three different magnetic phases. It was a 3D collinear antiferromagnet at temperatures below 214 K. When the temperature was raised, it first became an intermediate noncollinear incommensurate magnetic phase up to 230 K and then acted like a 1 D quantum antiferromagnetic material. The temperature dependent dielectric constant of polycrystalline \( \text{CuO} \) exhibits a striking feature of very high dielectric constant (\( \sim 2 \times 10^4 \)) comparable to those of the recently reported high dielectric materials \( \text{CaCu}_3\text{Ti}_4\text{O}_{12} \) (CCTO) and Li and Ti doped NiO (LTNO) ceramics. With regard to its commercial value, it has been widely exploited for use as a powerful heterogeneous catalyst to convert hydrocarbons completely into carbon dioxide and water. It is also potentially useful in the fabrication of lithium-copper oxide electrochemical cells [54]. Recently found that it is useful for supercapacitor application [55].

1.8.1 Crystal structure of \( \text{CuO} \):

The \( \text{CuO} \) has a considerably more complicated tenorite structure, similar to \( \text{AgO} \) [56]. The monoclinic unit cell (space group \( \text{C}_{2h}^6 \)) contains four molecules. The crystal parameters were measured to be \( a=4.6837 \text{ Å} \),
b=3.4226 Å, c=5.1288 Å, and β=99.54°. The coordination of atoms in CuO is such that each ion has four nearest neighbors of the other kind. In the (110) plane, each Cu atom is linked to four nearly coplanar O atoms at the corner of an almost rectangular parallelogram. The Cu-O bond lengths in this plane are 1.88 and 1.96 Å, respectively, which are larger than those in the cuprous oxide. The next to Cu-O bond lengths perpendicular to the plane are much greater, so an octahedral type of coordination can be ruled out. The O atom is coordinated to four Cu atoms in the form of a distorted tetrahedron. It is generally believed that the bonding in CuO is a mixture of ionic and covalent bonding, although the oxidation state of Cu in CuO is unquestionably Cu$^{2+}$. The transition-metal monoxides such as CoO and NiO, on the other hand, crystallize in the rocksalt structure with much higher symmetry. Thus, this may indicate a fundamental difference in electronic states between the CuO crystal and NiO or CoO crystal [57].

Fig. 1.11 Crystal structure of monoclinic CuO.

1.9 Carbon nanotube
Carbon nanotubes (CNT) are molecular scale tubes of graphitic carbon with outstanding properties. Sumio Ijima of NEC laboratory at Tsukuba first discovered and characterized CNTs structure [58]. His transmission electron microscopy (TEM) graphs revealed needle like materials were produced at the negative end of electrode during arc discharge evaporation of carbon and...
each needle comprised of coaxial tubes of graphite sheets. The multi-walled nanotubes contained at least two layers, often many more, and ranged in outer diameter from about 3 nm to 30 nm. They were closed at both ends. It maybe important to note, however, that nanoscale tubes of carbon, produced catalytically, had been known for many years before Iijima’s discovery. CNTs are among the stiffest and strongest materials known, and have remarkable electronic properties and many other unique characteristics. For these reasons they have attracted lots of academic and industrial interest, with thousands of papers on nanotubes being published every year.

1.9.1 Carbon Nanotubes Structure

The discovery of the C$_{60}$ molecule in 1985 by a group of chemists from Rice University (Texas, US) has evoked a tremendous interest among the world scientific community and lead to the development of a completely novel branch of chemistry called Fullerene- Chemistry [59]. Fullerenes are geometric cage –like structures of carbon atoms that are composed of hexagonal and pentagonal faces. Carbon nanotubes are long, slender fullerenes, in which the walls of the tubes are hexagonal carbon (graphite like structure), and the end caps contain pentagonal rings. CNTs were observed for the first time by Sumio Iijili in 1991 [58].

Theoretically, it is possible to construct carbon tubes by rolling up a hexagonal graphene sheet. In graphite, sp$^2$ hybridization occurs, where each atom is connected to three carbons ($120^\circ$) in the xy plane, and a weak $\pi$ bond is present in the z axis. The sp$^2$ set forms the hexagonal (honeycomb) lattice typical of a sheet of graphite [60]. The P$_z$ orbital is responsible for an van der Walls interactions. The free electrons in the P$_z$ orbital move within this cloud and are no longer local to a single carbon atom [61]. This phenomenon lies behind reason why graphite (and CNT, accordingly) can conduct electricity, as opposed to diamond, which behaves as insulator because all electrons are localized in the bonds within the sp$^3$ framework [62]. Besides being responsible for high conductivity, the delocalized $\pi$-electrons of carbon nanotubes could be utilized to promote adsorption of various moieties in the CNT surface via $\pi$- $\pi$ stacking interactions.
The exact properties of CNT are extremely sensitive to their degree of graphitization, diameter (or chirality), and whether they are in single wall or multi wall form. Single wall carbon nanotubes (SWCNT), which are seamless cylinders, each made of a single graphene sheet, were first reported in 1993 [63]. Multi wall carbon nanotubes (MWCNT), consisting of two or more seamless graphene cylinders concentrically arranged, were discovered two years previously.

Fig 1.12 Carbon nanotubes (a) a single wall carbon nanotube by rolling-up a graphene sheet (b) single wall carbon nanotube (SWCNTs) and (c) Multiwalled carbon nanotube (MWCNTs)
Three types of nanotubes are possible, namely armchair, zigzag and chiral nanotubes, depending on how the two dimensional graphene sheet is rolled up, as shown in the Fig. 1.13. The primary symmetry classification of a carbon nanotube is as either achiral or chiral. Both armchair and zigzag nanotubes are achiral since their mirror image has an identical structure to the original one. Chiral nanotubes exhibit a spiral symmetry whose mirror image can’t be superimposed to the original one. The different structure can be most easily explained in term of the unit cell of carbon nanotubes in Fig.1.14.

![Diagram of different types of carbon nanotubes](image)

**Fig 1.13 The different structure of carbon nanotubes**

The so-called chiral vector of the nanotube, \( \mathbf{Ch} \), is defined by \( \mathbf{Ch} = n \mathbf{a}_1 + m \mathbf{a}_2 \), where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are unit vectors in the two-dimensional hexagonal lattice, and \( n \) and \( m \) are integers. Another important parameter is the chiral angle, which is the angle between \( \mathbf{Ch} \) and \( \mathbf{a}_1 \). An armchair nanotube corresponds to the case of \( m=n \) and a zigzag nanotube corresponds to the case of \( m=0 \). All other \((n,m)\) chiral vectors correspond to chiral nanotubes [64] . The diameter of CNT, \( D_t \), can be calculated by \( L/\pi \), in which \( L \) is the circumference of the carbon nanotube:
\[ D_f = \frac{L}{\Pi} = a\sqrt{(n^2 + m^2 + nm)} \] (1.13)

Where the lattice constant \( a = 0.249 \) nm. For example, the diameter of the zigzag nanotube is \( D_f = 0.882 \) nm. The chiral angle \( \theta \) denotes the tilt angle of the hexagons with respect to the direction of carbon nanotube axis. It can be calculated by the following equation:

\[ \tan \theta = \frac{\sqrt{3}m}{2n + m} \] (1.14)

Fig. 1.14 Carbon nanotube lattice

### 1.9.2 Aggregation and poor solubility of carbon nanotubes

Nano-scale dimensions of CNT turn dispersion into a challenge, since as the surface area of particle increases, so does the attractive forces between the aggregates. High aspect ratios, combined with high flexibilities, increase the possibility of nanotube entanglement and close packing. The low dispersability stems from the tendency of pristine nanotubes to assemble into bundles or ropes, which contain hundreds of close-packed CNT tightly bound by van der Waals attraction energy of 500 eV/µm of tube – tube contact.
The solubility of carbon nanotubes may be necessary for their chemical and physical examination, since it allows easy characterization and facilitates their manipulation. Intensive research was addressed to overcoming the poor solubility of CNT in either water or organic solvents. The wetting properties of carbon nanotubes could be significantly improved via oxidation by strong acids, like H_2SO_4 or HNO_3, or mixture of acids [65].

1.9.3 Current approaches for dispersing carbon nanotubes:

Much effort has been investigated in developing approaches for reproducible dispersion of individual CNTs as stated earlier, in order to develop high property CNT based materials, fully utilizing unique properties of the tubes, the thermodynamic drive toward aggregation must be overcome. Therefore, dispersion method, as an integral step of the production chain, has to be selected in accordance with the processing condition of the CNT based material. Although the electronic properties of nanotubes are compromised via functionalization, their utility for rheological modifications of material blend remains profound. There are several approaches to introducing covalent site wall of functionalization of the tubes. These include the organometallic approach to product MWCNT with chlorinated polypropylene, fluorination with molecular and further substitution by alkyl groups and addition of nitrenes, carbenes, radicals etc.

There are two distinct approaches for dispersing carbon nanotubes: The mechanical method and methods that are designed to alter the surface energy of the solids, either physically (non covalent treatment) or chemically (Covalent treatment). Mechanical dispersion methods, such as ultra sonication (fig. 1.15) and high shear mixing, separate nanotubes from each other but can also fragment the nanotubes decreasing their aspect ratio [66].
In chemical method wetting properties of carbon nanotubes could be significantly improved via oxidation by strong acids, like H₂SO₄ or HNO₃, or mixture of acids [67]. The procedure results in the formation of carboxylic moieties, preferentially on the end caps of the CNT, since the regions where pentagons are located suffer more strain (higher chemical reactivity) compared with that of purely hexagonal lattice. Under these conditions, the end caps of the nanotubes are opened and acidic functionalities, which could be suitable for further derivatization (esterification or amidization), are formed at these defect sites and at the side walls.

Chemical methods use surface functionalization of CNT to improve their chemical compatibility with the target medium (solvent or polymer solution/ melt), that is to enhance the wetting or adhesion characteristics and reduce their tendency to agglomerate. However, aggressive chemical functionalization such as the use of neat acids at high temperatures might introduce structural defects resulting inferior properties of the tubes and is shown in fig 1.16.
Fig. 1.16 schematic presentation of chemical functionalization of carbon nanotubes.

Non-covalent treatment is attractive because of the possibility of adsorbing various groups on CNT surface without disturbing the π systems of the graphene sheets. In the last few years, the non covalent surface treatment by surfactants or polymer has been widely used in the preparation of both aqueous and organic solutions to obtain high weight fraction of individually dispersed nanotubes [69]. For example non-covalent modification of SWNT by encasing the tubes within micelles of cross-linked copolymer polystyrene-block-polyacrylic acid (PS-b-PAA) was demonstrated (Fig. 1.17) [70]. CNT were first ultrasonicated in DMF solution of the copolymer (Fig. 1.17, step 1) and micellization of the amphiphile was induced by adding water to the nanotubes suspension (step 2). Finally, the PAA blocks of the micellar shells were permanently cross-linked by adding a diamine linker (step 3). This encapsulation was shown to enhance the dispersion of SWNT in a variety of polar and nonpolar solvents. Fig.1.18 shows the mechanism of nanotube isolation from bundle obtained by ultrasonication and surfactant stabilization.
Fig. 1.17 Schematic presentation of non covalent functionalization

Fig. 1.18 Mechanism of nanotube isolation from bundle obtained by ultrasonication and surfactant stabilization
The capacitance of an EDLC is greatly influenced by the choice of electrolyte. The ability to store charge is dependent on the accessibility of the ions to the porous surface-area, so ion size and pore size must be optimal. The best pore size distribution in the electrode depends upon the size of the ions in the electrolyte, so both electrode and electrolyte must be chosen together.

The attainable cell voltage of a supercapacitor will depend on the breakdown voltage of the electrolyte, and hence the possible energy density (which is dependent on voltage) will be limited by the electrolyte. Power density is dependent on the cell’s ESR, which is strongly dependent on electrolyte conductivity. There are currently two types of electrolyte in use in EDLCs: organic and aqueous. Organic electrolytes are the most commonly used in commercial devices, due to their higher dissociation voltage. Cells using an organic electrolyte can usually achieve voltages in the range of 2 – 2.5 V. However, there are other considerations on the use of non-aqueous electrolytes such as high cost, low conductivity compared to aqueous electrolyte leading to power deterioration, low dielectric constant resulting in smaller capacitance, complex purification procedure as well as safety concerns due to the flammability and toxicity of the organic solvent. Ionic liquids (ILs), which are known as room temperature molten salts, are under considerable research for use as next generation electrolytes [71, 72]. They are attractive candidates for electrolytes used in energy storage because of their good chemical and physical properties, such as high thermal stability, high electrochemical stability over a wide potential window (43 V), non-toxicity, non-flammability, variety of combination choices of cations and anions, acceptable conductivity at elevated temperature, etc. ILs are liquids at ambient or even lower temperatures and are composed entirely of ions, making them attractive solvent free ‘green electrolytes’. But they are typically high viscosity liquids and have low ionic conductivity at room temperature, which inevitably affect their performance. Therefore, designing an IL with high conductivity and a large voltage window (44 V) for practical applications is still challenging. Given that high purity ILs are of great importance for long cycle lives of a supercapacitor, hydrophobic ILs are preferable due to a more readily
attainable high level of purity. It is worth noting that two principle factors are involved in the conductivity of the electrolyte system: (1) the ability of the salt dissociation to give out free charge carriers like cations and anions; and (2) the mobility of the dissociated ions in the electrolyte system. Hence, further research could be carried out to design ILs with a combination of ions having high dissociation constants, low molecular weight and with a wide electrochemical stability window. Although, with the currently available technology, ILs still fail to meet the requirements for practical applications, its future development will be of great significance in achieving high performance safe and ‘green’ energy storage systems.
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