Potential Transparent Supercapacitor Electrode Materials

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Abstract. Supercapacitor utilizes the nano-scaled pores to increase the surface area indefinitely and shortens the distance between the positive and negative plate, on the account that some larger particles cannot fit into the pores. According to the capacitance equation “capacitance = εε0 (area/distance),” as the distance decreasing and area increasing, the magnitude of the capacitance is tremendously magnified. A transparent supercapacitor describes a supercapacitor that has a high optical transmittance. If the intensity of light that transmits across the substance is higher than the rate that it is blocked or reflected. The substance possesses a transparency. The flexibility of transparent supercapacitors is another important area of studies. It generalizes a combination of stretchability, bendability, twistibility, or compressibility. In real life, it’s important to obtain the optimal optical transmittance, flexibility, and electrical conductivity for future devices such as smart glasses. These characteristics enable us to develop something more complex and advanced in the future.

1. Introduction
Transparent supercapacitor is a distinct type of supercapacitor that revolutionizes the electrochemical industry. It is developing toward computer glasses, wearing and portable electronics, or other highly advanced technological products. The transparency of an electrode material is directly proportional to its optical transmittance. Light waves with certain frequency strikes an object. If the object has the same frequency as the light, photons are absorbed and transformed into thermal energy of vibrational movement. The light waves pass through the object with minimum reflection, and re-emits on the other side of the object. This particular light wave is called transmitted light wave. Reports have shown that an underlying transparent indium - tin oxide layer [1] could provide efficient current collection and transparency. However, the element indium is expensive and unlikely to apply in the printed electronics in the future. Furthermore, its brittleness prevents applications where the flexibility of a supercapacitor is required. Graphene is a two-dimensional layer with sp2 hybridized structure. It has a strong mechanical strength, excellent flexibility, and good optical transparency. The implementation of chemical vapor deposition graphene film shows great stretchability and transparency. And the inexpensive synthesis of graphene film of inexpensive Ni and Cu foils is a desirable approach. A wrinkled structure of graphene [2] onto the polydimethylsiloxane (PDMS) showed less transparency and flexibility than that of the directly chemical-vapor-deposited layers of graphene film on the PDMS. Thus, the arrangement of graphene films also affect the transparency and flexibility of a supercapacitor. Carbon nanomaterials, generally have great flexibility and electric double-layer capacitance (EDLC) behaviours, showing wide applications in flexible supercapacitors. However, their optical transmittance is often limited by their low conductivity. It turns out its other replacement poly(3,4-
Ethylenedioxythiophene (PEDOT:PSS), a sprayed conductive macromolecular polymer, show more potential in the future mass production of transparent supercapacitors. PEDOT:PSS [3] is a versatile electrode film. It not only fits the biosensor supercapacitor (in which it traps the virus and tests if the sample from a patient is contaminated by cancer cells or viruses), but it is also suit, and commercially available for a transparent supercapacitor. The PEDOT:PSS’s volume alters the film transmittance, and the transparency increases with the film transmittance. Experiments show that PEDOT:PSS is essentially better than most graphene electrodes, on the account that its superior performance attributes as a transparent supercapacitor charge storage film to its low optical conductivity. The PEDOT:PSS on the electrode is spin-coated from a doped PEDOT:PSS solution. Various asymmetric supercapacitors electrodes or hybrid electrodes composed of PEDOT:PSS films show superior electrochemical behavior. Nevertheless, the thick PEDOT:PSS film layer conveys lower optical transmittance that is contrary to a transparent supercapacitor. The triangular Galvanic Charge-Discharge (GCD) shape of PEDOT:PSS indicates that it shows great capacitive behaviors as well. Polyvinylpyrrolidone (PVP) and LiClO₄ electrolytes can also serve as the coating of a transparent supercapacitor. PVP is an amorphous polymer. It has good stability and displays moderate ionic conductivity. Whereas the properties of PVP can change due to external factors, such as the increase of humidity and loss of residual solvents. These films have been employed in the fabrication of a symmetrical supercapacitor, which shows good transparency, capacitive behaviors, and some flexibility. The new devices illustrate the continued improvement in the development of transparent and flexible supercapacitors. In the future, researchers plan to further improve the energy density, flexibility, and durability, and stretchability of a supercapacitor.

2. Results and Discussion

2.1. Material
Material is the key indicator of the transparency, capacitance, and flexibility of a transparent supercapacitor electrode (TSE) material. Even though indium tin oxide (ITO) is still the most widely used TSE material nowadays, the material itself is brittle and expensive, which is not the most desirable material we want. Therefore, more materials emerge from studies of TSE around the globe. In general, the materials are categorized into two big groups. And these two groups extend many branches. The first big group is the distinct materials. This section is divided into five large groups: 1. ITO/FTO; 2. conductive polymers; 3. Metallic nanostructures; 4. Mxenes; 5. carbon materials. The second big group is categorized by the different chemical configurations of a material. The most usual material configuration that is implemented onto the TSC are the one-dimensional material (1D material), and two-dimensional material (2D material). Three dimensional materials (3D materials) are rarely used, but some of them convey really high flexibility and optical transmittance due to their unique mechanical and optical properties. For technological advancement in the future, we seek better and more robust TSC material every day.
Table 1. Properties of Different Transparent Supercapacitor Materials

| Electrode                        | Electrolyte       | Optical Transmittance | Voltage Window | Specific Capacitance | Cycling Stability | Energy Density | Power Density |
|----------------------------------|-------------------|-----------------------|----------------|----------------------|-------------------|----------------|---------------|
| ITO                              | [BMIM][Cl]RTIL    | 91.80%                | -0.5 - 0.5 V   | 22 F/g at 5 mV/s     | 111 F/g at 10 mV/s| 15.4 Wh/kg    | 7200 W/kg     |
| Graphene films                   | KCl               | 70%                   | 0 - 1 V        | 0.33 F/cm² at 10-500 mV/s | 15 F/g at 100 mV/s | 1.000 Wh/kg | 1.1 kW/kg     |
| CNC                              | PVA-H3PO4 gel     | 71%                   | 0 - 1 V        | 1235 F/g at 50 mV/s  | 10,000 cycles     | 47 mWh/cm³   | 19 mWh/cm³    |
| PEDOT                            | PVP-LiCO3         | 50%                   | -1 - 1 V       | 15 F/g at 100 mV/s   | 1.400 cycles       | 4.000 Wh/kg  | 16.0 Wh/kg    |
| Highly aligned CNT               | PVA               | 75%                   | 0 - 0.8 V      | 7.3 F/g at 10 V/s    | 2.000 Wh/kg       | 1.000 Wh/kg  | 1.100 kW/kg   |
| RuO2–ITO                         | H2SO4             | 0.3 - 0.8 V           | 1235 F/g at 50 mV/s | 4.000 cycles     |                   | 1.000 Wh/kg  | 1.100 kW/kg   |
| Freestanding and flexible graphene membrane | PVA | 59% | 0 - 1 V | 55 F/g | 20,000 cycles | 430 μWh/cm³ | 190 mWh/cm³ |
| AACS nanowires                   | Polymer electrolyte | 85% | 0 - 0.8 V | 136.5 μF/cm² |                   | 1.000 Wh/kg | 1.100 kW/kg |
| PSC/MAM                          | PVA/H2SO4         |                       | 459.6 F/m²     | 35.9 mWh/m²         | 461.5 mWh/m²      | 1.000 Wh/kg  | 1.100 kW/kg   |
| MoO3 nanobelts                   | LiCl              | 90%                   | 0 - 0.8 V      | 1198 F/g at 2 mV/s   | 20,000 cycles (96.5%) | 22.89 Wh/kg | 686.84 W/kg |
| Co3O4 nanocrystal                | PVA/H3PO4         | 51% at 550nm          | 0.2 - 0.6 V    | 177 F/g at 1 mV/s    | 20,000 cycles (100%) | 3.01 Wh/kg | 1.152 kW/kg |
| MnO2@Ni                          | Na2SO4            | > 84%                 | 0 - 0.8 V      | 131.5 mF/cm² at 100 mV/s | 10,000 cycles (96.3%) | 1.000 Wh/kg | 1.100 kW/kg |
| Inject printed graphene          | H3PO4             | 87% at 550 nm         | 0 - 1.0 V      | 8.7 μF/cm² at 50 mV/s | 10,000 cycles (91.3%) | 1.000 Wh/kg | 1.100 kW/kg |

ITO is widely used due to its high optical transmittance and electrical conductivity. It comprises of 74% In, 18% O2, and 8% Sn by weight. Its conductivity comes from the metallic bonds of indium doped tin oxide. On the other hand, its transmittance is high owing to its high light-scattering haze factor, which is the ratio of transmitted light and reflected light. The material looks like a piece of glass. Fluorine tin oxide (FTO) shares similar properties with the ITO. In further lab research, a solid-state flexible supercapacitor with room temperature ionic liquid gel, and ITO electrodes is found by researchers to be safe, environmentally friendly, flexible, and transparent. [BMIM][Cl] is used as the solvent, and ITO is coated onto the polyethylene naphthalate (PEN) [4]. Moreover, ITO is immensely used as the material for the touch screen of a smartphone. Conductive polymers are another important material in the...
fabrication of TSE. They are characterized as robust, transparent, and highly conductive. Polymers are long organic chains. Picture a polymer as countless joints connected, since these are monomers with only a few nanometers. These joints give it multiple pivot points that enable it to move around quite easily. Therefore, Young’s modulus of the polymer materials is relatively high, which means it has high flexibility. Polymers are transparent because the light can transmit through certain plastic materials. For example, polyethylene terephthalate (PET) is a common material to fabricate plastic bottles. Some polymers take thousands of years to decompose, which is environmentally unfriendly, so it’s essential to choose the polymer materials we want wisely. The potential use of PEDOT: PSS conductive polymer films on a TSE intrigues many researchers. The PEDOT: PSS coated transparent supercapacitor has electrodes that are 95% transparent, and a capacitance of 12 mF at a scan rate of 50 mV/s. Its capacitance is much higher than any previously reported transparent supercapacitor. PEDOT: PSS polymers are commercially available, unlike the expensive ITO. These polymers have good transmittance due to their low optical conductivity. They are easily adjustable through doping. For example, their sheet resistance decreases dramatically after a small modification. In the meantime, its capacitance is maximized. An aqueous dispersion of PEDOT: PSS is used to create PEDOT: PSS films on PET substrates. Films are prepared after a formic acid post-treatment. A free-standing PEDOT: PSS electrodes not only have superior electrochemical performance and high flexibility but also excellent electrochemical performance in a flexible and transparent all-solid-state supercapacitor. Its 2 vol% surfactant (Triton-X 100) [5] enhances the electrical conductivity, improves the wettability, and reduces the surface tension, which is favorable for the multilayer spin coating of the PEDOT: PSS films to form a smooth and uniform surface morphology. PEDOT: PSS electrodes with one layer were fabricated via spin coating the resulting formulation on PET substrates at 500 rpm for 6s. The gel electrolyte was then coated on the PEDOT: PSS/PET. Most polymers are not electrically conductive by itself. However, if a thin sheet of metal is usually deposited onto the polymer, it enables them to convey both high flexibility and high electrical conductivity. This is where the third material nanostructures come in place. We create metallic nanowires on the surface of a substrate. The substrate is usually polymer to maximize its conductance. The thickness of the substance is inversely proportional to its reluctance. Thus, its thickness must be right to convey the maximum conductivity and transparency at the same time. The polymer can exist as either the current collector or the electrolyte to maximize the conductivity of a TSE. For instance, a supercapacitor based on electrochemically stable Ag–Au-core−shell nanowire percolation network electrode [6] has an excellent electrical conductivity as well as greatly enhanced chemical and electrochemical stabilities. Ag–Au-core−shell is synthesized through a simple Au coating process in the solution environment. Polyvinyl alcohol (PVA) serves as its electrolyte, and this sort of supercapacitor exhibits no degradation upon repeating the charge-discharge cycle. Nevertheless, the substrate can be other materials such as manganese oxide, which also conveys good transparency and flexibility. The researchers developed a novel Au@MnO2 core-shell nanomesh structure [7] on a flexible polymeric substrate through nanosphere lithography combined with electro-deposition processing. The direct growth of MnO2 on gold nanomesh increases the transparency and achieves an efficient contact between the current collector and active materials. As a result, it has a high areal capacitance of 4.72 mF/cm2. Ultimately, the research of metallic nanostructures is another way to approach a perfect TSE. MXenes is different from metallic nanostructures. Even though MXenes contain metal compounds and are electrically conductive, it is, in fact, a 2D transition metal carbides and nitrides which have displayed promising properties in numerous applications, such as energy storage, electromagnetic interference shielding, and catalysis. A transparent, flexible, and conductive 2D titanium carbide (MXene) films display high volumetric capacitance [8]. Its layered structure creates a good condition for intercalation reaction to take place. Therefore, it has a high energy density due to its high pseudocapacitance, and meanwhile a high power density. Last but not least, carbon materials are the second most abundant TSE materials due to their practicability. They are characterized as highly flexible and conductive. Furthermore, 1D and 2D carbon materials show how different arrangements of materials can affect the property of that material. Carbon nanotube (CNT) [9] is a common 1D carbon material. As its name suggests, it’s a tubular structure. When trillions of these tubular structures are interconnected, it forms
a giant network. As a result, when the network is disturbed by a force, it can disperse the pressure into multiple units, and therefore, very flexible. Single-walled carbon nanotubes (SWCNTs) [10] are particularly attractive replacement of ITO. A solution-based deposition is the main method for fabricating SWCNTs transparent and conductive films (TCF) because it is low-cost and scaled up to large areas. Chemical vapor deposition technique fabricated transparent and conducting SWCNTs films. It decreases the surface resistance and increases power density. On the other hand, 2D material is a flexible material by itself. Graphene is a good example. It has multiple ring structures and shows high tensile strength. Each ring acts as a joint that disperses the outside force, as the CNTs. Moreover, it has free electrons all over the place due to its resonance structure. Therefore, it conveys a high electrical conductivity on the account that currents can flow across its surface or interior easily. A laminated ultrathin chemical vapor deposition graphene films based [11] stretchable and transparent high-rate supercapacitor is stretchable and transparent. Its electrode is made of four-layer laminated ultrathin graphene films. Specifically, It has an optical transmittance of 72.9%, and a stretchability of 40%. Its specific capacitance (5.33 μF/cm2 at 200 mV/s) showed no degradation and even increased slightly over 10,000 cycles. The weak D band of these layers of graphenes suggests that neither stretching or processing induces mechanical damages to the buckled graphene films. Furthermore, a wavelength of 550 nm (within the range of visible lights) gives the material its transparency. A single layer graphene film was synthesized using chemical vapor deposition methods. The laminating procedure stacked single-layered graphene layers into polymethyl methacrylate (PMMA). The H2SO4 electrolyte is then prepared and coated on the electrode.

2.2. All in one device
One way to further improve the TSE is to make a hybrid electrode material that takes the advantages of different materials. The reason that we add metallic nanowires onto a thin polymer sheet is that we want the optimal electrical conductivity, optical transmittance, and flexibility altogether. Vertically aligned ZnO@CuS@PEDOT core@shell nanorod arrays [12] decorated with MnO2 nanoparticles for a high-performance and semi-transparent supercapacitor electrode is a good example. Hybrid nanoarchitectures with high electrochemical performance for supercapacitors have been designed by growing hierarchical ZnO NRs@CuS@PEDOT@MnO2 core@shell nanorod arrays on ITO/glass substrates. These 1D semiconducting ZnO structures have a high aspect ratio, high surface area, and very high crystalline quality and can provide a direct conduction path for electrons. These advantages contribute to an areal capacitance of 9.85 mF/cm2 at 100 mV/s, and a power density of 10 kW/kg.

3. Conclusion
The two main characteristics of a future supercapacitors are flexibility and transparency. In particular, its flexibility comes from flexible materials such as conductive polymers and carbon materials. Even though conductive polymers are usually not stable under high temperature or high humidity, which leads to short cycle lives, they can be readily manufactured, and chemical doping strengthens their stability. Moreover, these conductive polymers have long chains and strong bonding. As a result, conductive polymers are typically more elastic than other materials. On the other hand, there are multiple kinds of polymer materials. They can be either amorphous or crystalline. Amorphous polymers are generally more transparent than crystalline polymers due to their near-zero light refraction. Nevertheless, it’s possible to make these crystalline polymers transparent. One way to achieve that goal is to create ultrathin film of these polymers. In the meantime, it’s important to make sure the crystals inside these crystalline polymers are oriented in a way that the size of the crystals become smaller, on the account that smaller crystals do not cause the refraction of light rays. Furthermore, an additive technology also improves the transparency of crystalline polymers. The injection of a metallocene catalysts can potentially increase the transparency of a polymer film due to a decrease in the degree of crystallinity. Still one thing to notice here, at a temperature of about 120 - 130 °C, the sample will begin to form a haze caused by the crystal formation. It’s still under investigation how to preserve the properties of conductive polymers we want under extreme conditions. Carbon materials are also an excellent
candidate for a transparent flexible supercapacitor. 1D and 2D carbon materials both convey high flexibility. CNTs are the most common flexible supercapacitor electrode material in 1D carbon. One CNT is neither flexible nor a good material for an electrode material, but if you “stitch” trillions of these CNTs together. A CNT network forms. Each of the CNTs act as a mechanical joint, therefore, the Young’s modulus of CNT network material is particularly big. Likewise, 2D carbon materials utilize this mechanical property as well. For example, the hexagonal ring structures on graphene molecular configuration also act as joints. In contrast, 2D carbon graphene is already a flexible material by itself. Graphene also has a large surface area in contact with the electrolyte. Therefore, graphene electrode material conveys a large capacitance [13]. However, these two materials are not perfect. Both of them are difficult to be processed in solution because of their low solubility in most solvents with no treatment. Moreover, graphene is susceptible to re-stack over cycles [14]. As a result, its active surface area is limited and it lowers the actual capacitance of graphene electrode in comparison to its theoretical capacitance. MXene is a 2D transition metal carbide/nitride. It’s another excellent 2D electrode material for a flexible supercapacitor. Graphene and MXene both have good electrical conductivity, on the account that graphene has free electrons moving around, and MXenes have metallic intermolecular bonding. The high conductivity enables these two materials to have stronger currents, and thus, higher power density. In addition, MXenes have solid’s layered structures. Because of that, more intercalation reactions can take place within the supercapacitor, which leads to a high pseudocapacitance. Even though carbon materials and MXene are so desirable flexible materials, their thickness must be thin enough to make these materials transparent. And problems come along. When these materials are much smaller than they were before, their tensile stress limit decreases and resistance increases owing to the decrease in thickness. The same issue falls on another candidate of transparent supercapacitor electrode. Metallic nanostructures make full use of ultrathin metals (nanowires and nanopores) to tremendously increase the electrode surface area, and it has high electrical conductance as MXenes. Nevertheless, thin metals are less reactive, and get oxidized quickly when it’s exposed to air. To tackle the conundrum, a possible solution is to a tolerant polymer film such as PET under these materials. It will prevent the materials from losing the quality they had before, and increase the optical transmittance of the material.

It’s now time to take real consideration of the all in one devices. Almost no materials are perfect alone, but if you choose the proper materials and combine them together. Their advantages will compensate their disadvantages. Hybrid supercapacitor electrode is the future of supercapacitor businesses. It will enable us to build better interactive devices such as smartphones, smart windows, smart glasses, tablets, and other touchable devices. In other words, the assembly of different materials maximize the functionality of a transparent supercapacitor devices. It merges the electrical conductivity, optical transmittance, and mechanical properties.

- Compositing electrode materials make the best combination of high performance
- Highly transaprent and flexible electrolyte with safe and ionic conductive are to be studied,
- Metrics of quantifying transparency and flexibility of supercapacitors are to be developed.
- Lowering the cost;miniaturizing the device
Fig. 1 Transparent Conductive Electrodes

In that way, future technologies like hologram will show up in the near future because of the fabrication of an almost perfect transparent supercapacitor.

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