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(54) Title: PROTECTIVE COATINGS FOR POROUS CONDUCTIVE FILMS AND COATINGS

(57) Abstract: The present invention relates to a class of metal salt precursors that can be combined with carbon nanotube conductive layers for improvement of performance characteristics and to methods for making and using these combinations. In particular, the invention is directed to precursors that are deposited onto CNT as binders, films, coatings, protective layers, and top coats comprising the oxo-alkoksosalt, metal oxosalts or metal oxides.

Figure 1. 100 deg heat stability of CNT/oxosalt IuCB composition on glass (ldip).

15% In Cl3 sol. on glass

- CNT/In Cl-8
- CNT/In Cl-1*
- bare CNT contr.-1*
- bare CNT Cl-7

Relative Rs Increase

Rstar: 120

Storage time, hours

-0.1
0
0.2
0.4
0.6
0.8
0.9

0
144
260
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PROTECTIVE COATINGS FOR POROUS CONDUCTIVE FILMS AND COATINGS

Rights in the Invention

This invention was made, in part, from support provided by the United States Department of Energy under Grant No. DE-FG36-05GO85035 and, accordingly, the United States government has certain rights in this invention.

Reference to Related Applications

This application claims priority to United States Provisional Application No. 60/876,165, filed December 21, 2006, entitled "Protective Coatings for Porous Conductive Films and Coatings," which is specifically and entirely incorporated by reference.

Background of the Invention

1. Field of the Invention

The present invention relates to a class of precursors that can be combined with carbon nanotube conductive layers for improvement of performance characteristics and to method for making and using these combinations. In particular, the invention is directed to precursors that are deposited onto CNT as binders, films, coatings, protective layers, and top coats comprising the oxo-alkokso-salts, metal oxosalt or metal oxides.

2. Description of the Background

Successful and practical sol-gel coatings today have been realized in electronics, optics, automotive, chemical and food industries. Among these materials one can identify ferro- and piezo-dielectrics, solid electrolytes, refractory materials, membranes, protective coatings and films with special optical and electro-physical properties. Carbon nanotube (CNT) containing conductive layers are coated with metal oxides using advantages presented by sol-gel method for creating composites with exceptional performance characteristics (see e.g. U.S. Patent Nos. 4,874,462; 5,137,749; 6,355,821; 6,965,006; 6,988,925; 6,596,807; 7,060,241; 7,118,693; U.S. Patent Publication Nos. 20060113510; 20060111008; 20050221016; 20050209392 and Turova, Turevskaya, Kessler, and Yanovskaya, The Chemistry of Metal Alkoxides, Kluwer Academic Publishers, Boston, 2002) (all of which are hereby specifically and entirely incorporated by reference).

Numerous electronic devices require electrical conductors which are optically transparent to visible light. The transparent electrical conductors function by transmitting electrical power to operate user interfaces like touch screens or to send a
signal to a pixel in an LCD display. Transparent conductors are an essential component in many optoelectronic devices including flat panel displays, touch screens, electroluminescent lamps, solar panels, "smart" windows, and OLED lighting systems. In all these applications, the user must see through the conductive layer to perform an operation. In addition, transparent patterned conductors are valuable in making biometric identification cards, e.g., Smart cards in which the information is stored in or transferred thought the conductive layer. The use of transparent conductive layers in such cards is advantageous for security purposes since it is difficult to find the information.

Today most transparent electrodes are made from transparent conducting oxides, such as indium tin oxide (ITO), and have been the preferred choice for four decades. ITO is applied to an optically transparent substrate by vacuum deposition and then patterned using costly photolithographic techniques to remove excess coating and form the wire and electrodes. Both of the processes are difficult and expensive to scale up to cover large areas. ITO also has some rather significant limitations: 1) ITO films are brittle (mechanical reliability concern for flexible applications such as in plastic displays, plastic solar voltaic, and wearable electrical circuitry); and 2) ITO circuits are typically formed by vacuum sputtering followed by photolithographic etching (fabrication cost may be too high for high volume/large area applications).

Efforts have been made to provide transparent electrodes to replace ITO film. A typical example is a suspension of ITO particles in a polymer binder. However, this ITO-filled system cannot match the electrical conductivity of a continuous ITO film. Furthermore, transparent conductive polymer materials are now being developed. These polymers typically require dopants to impart conductive properties and are applied on a substrate using screen printing or an ink jet application technique. Although they are still at a development stage, and have yet to reach the conduction level of an ITO film, the presence of dopants has an adverse effect on making these materials sensitive to environmentally induced changes in resistance and transparency.

Future electronic devices are limited in function and form by the current materials and processes utilized to create electrically conductive transparent layers. The need for electrically conductive optically transparent coatings and films continues to increase. These films and coatings need to be more transparent and at least equally conductive. Such films are preferably processed using large area patterning and ablative techniques, as well as being flexible and wholly low in cost.
Metal oxide coatings have been identified previously, for various purposes. For example, Shibuta (U.S. Patent No. 5,908,585) discloses a transparent electrically conductive film having a surface resistivity of $10^2$ to $10^{10}$ Ω/n, a light transmittance of at least 70%, and a haze value of at most 20% and comprising an organic or inorganic transparent matrix having dispersed therein 0.01%-1 wt % of hollow carbon microfibers and 1%-40 wt % of an electrically conductive metal oxide powder (such as antimony-doped tin oxide) with an average primary particle diameter of 0.5 μm or smaller. The matrix can be an organic polymer which is thermoplastic, thermosetting, or curable by ultraviolet radiation, or a metal oxide sol which can form an inorganic glass film, a hydrolyzable or heat decomposable organic metal compound, or the like.

Shibuta, however, fails to identify the specific materials which are effective at providing protection (since not all metal oxide sols are effective) or application methods as described in the instant application. This is not surprising since Shibuta only worked with blends of large diameter nanotubes (i.e. multi-walled nanotubes (MWNT) or fibrils) with binder materials, and this particular form of carbon nanotubes does not exhibit the same environmental sensitivities that occur in smaller structures such as single-walled carbon nanotubes (SWNT) and nano-structured metal coatings. Shibuta is also limited to blending metal oxides directly within the MWNT or fibrils, which is not optimal for reducing resistance and enhancing optical transparency. Shibuta is further limited to classic silica gel chemical pathways to achieve its metal oxide containing coatings.

U.S. Patent No. 6,713,947 also discloses certain metal oxide uses, and is directed to a display device that can realize efficient electron emission characteristics by ensuring the exposure of carbon nanotubes in the inside of a vacuum by fixing the carbon nanotubes to cathode wires such that the carbon nanotubes are not easily removed from the cathode wires with the small resistance which enables the carbon nanotubes to have the enough electron emission ability. In that patent disclosure, the inventors describe the use of metal oxides as a binder to attach carbon nanotubes (CNT) to a conductive substrate so as to fix them in the z-direction of the plane of the substrate. However, that patent is not directed, nor does it suggest applying the binder so as to offer advantages such as increased surface conductivity, optical transparency, or environmental protection, among others. Furthermore, the chemical methods disclosed in U.S. Patent No. 6,713,947 to make the binder do not offer advantages such as low cost, simplicity of deposition and of processing methods.
Carbon nanotube (CNT) conductive films when combined with oxo-alkoxosol metal salt derivatives offer additional advantages to those presented by sol-gel methods for creating composites with improved performance characteristics at low cost. Previously, Han and Zettl disclosed deposition of tin oxide from a solution of tin (II) chloride onto single-walled nanotubes (Nano Lett, 2003, 3, 681-683). This reference was not directed to formation of a conductive network, and only focused on depositing particles into a CNT dispersion in an aqueous solvent. Further, the reference was not directed to studying the electronic, optical, or sensitivity properties of tin oxide on carbon nanotubes, but suggested that tin oxide coated carbon nanotubes could act as nanoscale sensors in, for example, molecular detection and "transduction." This work was directed to increasing, rather than decreasing, sensitivity to environmental exposure of carbon nanotubes. Thus, Han and Zettl took advantage of carbon nanotubes' tendency to lose resistance in response to exposure to various environmental factors.


Summary of the Invention

The present invention overcomes the problems and disadvantages associated with existing nanotube coatings and designs, such as changes to electrical resistance during or after exposure to environmental conditions, like humidity, high temperature, and/or electromagnetic radiation exposure such as UV light. These are commonly experienced environmental conditions for typical electronic devices including consumer


electronics such as touch screen-based PCs or PDAs and in other electro-optical devices such as solar cells and information displays which may all comprise nanotubes coatings as electrodes or to form conductive circuits.

It was surprisingly discovered that specific inorganic metal oxides, and combinations thereof, can be formed over a preexisting network of carbon nanotubes, preferably single-walled carbon nanotubes, producing novel materials with unique properties including improved stability of electrical, chemical and physical characteristics upon exposure to a plethora of environmental conditions.

One embodiment of the invention is directed to a composite comprising an electrical network and a network of amorphous metal oxide, as an insular, wherein the composite is electrically stable, and wherein the metal oxide is formed from a precursor selected from the group consisting of an oxo-alkokso-salt, a metal oxosalt, and combinations thereof. Preferably, the surface resistance of the composite undergoes a less than 25%, less than 20%, less than 15%, less than 10%, or less than 5% change, or no detectable or significant change upon exposure to temperatures of 80°C or greater, electromagnetic radiation, UV radiation, a relative humidity of 15% or greater, physical stress, chemical stress, mechanical stress. Also preferably, the composite has a thickness, a length and a width, wherein the length to thickness ratio is 100,000 or greater, wherein the width to thickness ratio is greater than 100,000, or combinations thereof. Alternatively, the thickness of the composite is preferably less than 500 nm, less than 200 nm, or less than 100 nm. Preferably, the electrical network is comprised of single walled carbon nanotubes, double walled carbon nanotubes, multiwalled carbon nanotubes, graphite, graphene flakes and sheets, amorphous carbon, gold nanowires, silver nanowires, nickel nanowires, platinum nanowires, InP nanowires, Si nanowires, GaN nanowires, nanoporous gold, nanoporous silver, nanoporous platinum, nanoporous palladium, nanoporous copper, nanoporous nickel, gold, silver, platinum, palladium, copper, nickel, iron, cobalt, yttrium, indium tin oxide, antimony tin oxide, aluminum doped zinc oxide, indium zinc oxide, transparent conductive oxides, semi-metals, alkalis, alkaline earths, lanthanides, actinides, transition metals, poor metals, metalloids, alloys of any of the foregoing, or combinations thereof. Also preferably, the carbon nanotubes of the composite are substantially uniformly distributed, substantially aligned, substantially disentangled, or combinations thereof.

In a preferred embodiment, the carbon nanotubes of the composite have aspect ratios of 1-100, 100-1000 or greater than 1000 and forms ropes and snakes, and
preferably has an optical transparency of greater than 60%, greater than 70%, greater than 80%, greater than 90%, greater than 95% or about 100%. Preferably, the composite has a surface resistance of less than $10^6 \, \Omega$/square, less than $10^5 \, \Omega$/square D, less than $10^4 \, \Omega$ square / square $\pi$, less than $10^3 \, \Omega$/square D, less than $10^2 \, \Omega$/square D, or less than $10 \, \Omega$/square D. Preferably, the precursor comprises a metal salt containing Al, Zn, Ti, Si, Sn, Bi, In, Pb, Cr, Nb, Ta, V, Sc, Ln, Mn, Mo, W, Co, Ni, Cu, Ge, Ga, Zr, Mg, Ba, Fe, chloride, fluoride, iodide, bromide, acetate, propionate, carboxylate, organic anions or combinations thereof.

In another embodiment, the network of carbon nanotubes and the network of metal oxide are continuous and porous, and wherein the continuous and porous network of carbon nanotubes interpenetrates with the continuous and porous network of metal oxide to form a continuous and porous composite network. Preferably, the composite comprises a substrate selected from the group consisting of polymer film, glass substrate, polymer, polyester, polycarbonate, polyolefin, polyurethane, acrylate, epoxy, fluorocarbon elastomer, plastic, thermoplastic, polyethylene tetraphthalate, polyethylene naphthalate, and combinations thereof. Also preferably, the composite comprises one or more layers containing the amorphous metal oxide. In another embodiment, the one or more layers containing the amorphous metal oxide have a surface resistance of greater than $10^7 \, \Omega$/square D, greater than $10^{10} \, \Omega$/square D, greater than, greater than $10^{12} \, \Omega$/square D, or greater than $10^{20} \, \Omega$/square C.

In another embodiment, the composite comprises a separate layer containing the carbon nanotubes, and wherein the surface resistance of the one or more layers containing the amorphous metal oxide to surface resistance of the layer containing the carbon nanotubes ratio is greater than 10, greater than $10^2$, greater than $10^5$, or greater than $10^7$. Preferably, the composite further comprises a polymer selected from a group consisting of polyester, polyurethane, polyolefin, fluoroplastic, fluoroelastomer, thermoplastic elastomer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, polyvinylalkyl vinyl ether, a melamine/acrylic copolymer, UV curable epoxy, a copolymer or polymer mixture, and combinations thereof.

Another embodiment of the invention is directed to a method of forming an electrically conductive and transparent film comprising: providing an electrically conductive network of carbon nanotubes; and depositing a metal salt solution comprising an alcohol and an acid onto the network, wherein the metal salt undergoes hydrolysis to be converted to a metal oxide. Preferably, the method further comprises
air drying the film and the depositing of the metal salt solution comprises dip coating the network into the solution. Also preferably, the method further comprises heating the film at a temperature of between approximately 60 and 200 degrees Celsius, wherein heating is performed for more than 15 minutes, more than 30 minutes, more than 1 hour, more than 1.5 hours, more than 2 hours, more than 2.25 hours, more than 2.5 hours.

In another embodiment, the method further comprises depositing a polymeric coating on the composite, wherein the polymeric coating comprises polyester, polyurethane, polyolefin, fluoroplastic, fluoroelastomer, thermoplastic elastomer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, polyvinylalkyl vinyl ether, a melamine/acrylic copolymer, UV curable epoxy, a copolymer or polymer mixture, or combinations thereof. Also preferably, the polymeric coating is adhesive, prevents degradation of the composite due to mechanical or physical stress, or has an index of refraction which matches adjacent layers.

In another embodiment, the depositing of the metal salt solution is repeated after the air drying. Preferably, the surface resistance of the film undergoes a less than 25%, less than 20%, less than 15%, less than 10%, less than 5% change or no detectable or significant change upon exposure to temperatures of 80°C or greater, electromagnetic radiation, UV radiation for more than 100 hours, a relative humidity of 15% or greater, physical stress, chemical stress, mechanical stress. Also preferably, the metal salt solution comprises wherein the precursor comprises a metal salt containing Al, Zn, Ti, Si, Sn, Bi, In, Pb, Cr, Nb, Ta, V, Sc, Ln, Mn, Mo, W, Co, Ni, Cu, Ge, Ga, Zr, Mg, Ba, Fe, chloride, fluoride, iodide, bromide, acetate, propionate, carboxylate, organic anions or combinations thereof. Another embodiment of the invention is directed to a composite formed by the method of the invention.

Another embodiment of the invention is directed to a method of patterning an electrically conductive and transparent coating comprising: depositing a layer of carbon nanotubes onto a film; selectively depositing a metal salt solution onto a portion of the layer of carbon nanotubes; heating the film comprising the carbon nanotubes and the metal salt solution; and removing a portion of the carbon nanotubes onto which the metal salt solution was not deposited to form a pattern.

Other embodiments and advantages of the invention are set forth in part in the description, which follows, and in part, may be obvious from this description, or may be learned from the practice of the invention.

Description of the Figures
Figure 1 depicts 100 deg heat stability of CNT/oxosalt InCl3 composition on glass (ldip).

Figure 2 depicts 100 deg heat stability of CNT/oxosalt InCl3 composition on PET (1 dip).

Figure 3 depicts 100 deg C Heat Stability of CNT/salt metals composition on glass.

Figure 4 depicts 100 deg C Heat Stability of CNT/salt metals composition on PET.

Figure 5 depicts 100 deg C heat stability of CNT/Multilayer Hybride Salt metal coating where Indium oxosalt is added first, followed by tin oxosalt addition.

Figure 6 depicts 100 deg C Heat Stability of CNT/Metal Alkoxides and Salt metal (Zn(OAc)2) composition on PET. Al and Ti alkoxides were deposited first using one dip, and the Zn acetate was deposited as a second layer.

Figure 7 depicts 100 deg C Heat Stability of CNT/metal alkoxides and metal oxosalt (ZnCl2) composition on PET. Al and Ti alkoxides were deposited first using one dip, and the Zn chloride was deposited as a second layer.

Description of the Invention

It is desirable for many applications to provide protection to thin porous coatings from the deleterious degradation in properties when in use or exposed to processing conditions. It was surprisingly discovered that a new class of compounds that can be used as precursors for creating composites with transparent carbon nanotube films and nanostructured conductive coatings with improved optical, electrical, and mechanical properties.

Many multifunction coatings are used in products today and are recently being fabricated using materials structured or formed from nano-scopic sized particles such as carbon nanotubes, metals, and ceramics. The small thickness (typically <200 nm) and porous nature of these coatings makes them susceptible to damage from the environment or during processing in the factory. Specifically such thin coatings or films can be damaged by abrasion, radiation, humidity, high temperatures, thermal cycling, delamination, bending, folding, creasing, and many other common environmental conditions where thicker coatings are not susceptible to degradation or protect the substrate from damage. This invention provides a coating material that protects very thin porous coatings or films from damage while being applied at a thickness far lower than traditional protective coatings and in addition, can enhance the performance of
characteristics such as electrical conductivity, optical transparency, or surface roughness. This invention is preferably directed to the use on transparent conductive coatings comprised of nanotubes, nano porous metals, nanoporous refractory materials, nanoparticle-based conductive oxides, and conductive polymers. The addition of the metal oxosalt coatings according to certain embodiments, to any one or combination of these conductive layers provides surprising and unexpected benefit to the electrical and optical characteristics which made these transparent conductive coatings useful initially.

The most commonly used precursors for preparation of metal oxides by the sol-gel method are metal alkoxides. Salt of metals dissolved in alcohols can be used as a starting material, as well and allow the formation of unique composite materials when combined with nanostructured conductors. However, the use of metal salts to make composite coatings according to certain embodiments of the present invention has advantages over the use of metal alkoxides in many cases.

The present invention relates to a new class or classes of precursors that are used in combination with CNT conductive layers for improvement of performance characteristics when the precursors are deposited onto the CNT as binders, films, coatings, protective layers, and top coats comprising the oxo-alkokso-salts, metal oxosalt or metal oxides. In one embodiment, film former (sol), comprising one or more salt metals is deposited onto an existing carbon nanotube (CNT) layer or can be blended together into a formulation prior to deposition on the substrate. Upon deposition, the solvent preferably evaporates leading to formation of a film of oxo-alkokso-salts metal derivatives. In another embodiment, baking or heating of such films leads to final removal of residues and impurities, including, but not limited to alkoksyl, hydroxyl groups, HCl, acetic acid, solvent, and water. In some embodiments, the oxosalts interpenetrate the CNT network to form the corresponding composite. If a substrate is present, the coating also preferably penetrates to the substrate through the CNT network and bonds the entire composite to the substrate.

In some embodiments, the salt-CNT composite can be coated with other binders (see U.S Patent Applications 200601 13510 and 20050209392) since if low levels of the metal oxosalt coating are used this will leave the coating layer porous and open to a third material to infiltrate the resulting composite. The method and materials of forming binders, films, coatings, protective layer, and top coats from metal oxosalts differs from the use of metal alkoxides, also known as the sol-gel method. In particular, those skilled in the art will recognize that the chemical pathways associated with metal oxosalts differ
from metal alkoxides to make a metal oxide or metal oxosalt coating. However, in certain embodiments, these two chemistries can be used in combination, where a metal alkoxide forms a sol with metal oxosalt present in the solution.

Certain embodiments are directed to applying a binder to an existing layer of essentially pure nanotubes, nanoparticles, or a nanostructured coating to form a composite in two steps, thereby maximizing the physical connections in the conductive network and minimizing the thickness of the composite. Thus, the present invention provides enormous advantages over the common blending directly with the conductive phase (typical of the prior art in the field) in terms of exploiting the benefits of reduced resistance and enhanced optical transparency.

Commonly, precursors for sol-gel methods are metal alkoxides. However, in certain embodiments of the present invention, metal salts, being dissolved in alcohols, can be used as starting material. Dissolution of salts, formed by cation of weak base and anion of strong acid usually is accompanied by vigorous reaction, leading to alkoxochloride. In certain embodiments, dissolution of metal salts is accompanied by a vigorous solvolysis reaction. Salts such as metal halogenides, being strong Lewis acids, demonstrate a tendency to undergo solvolysis, which increases from primary alcohol to secondary and tertiary. The dissolution of ZnCl₂ in alcohol, for example, accompanied by formation of zinc alkoxochloride-ZnCl₂(n)₂-n, evolution of HCl, and followed by further reaction ROH + HCl =RC1 + H₂O. This reaction is catalyzed by ZnCl₂(n)₂-n.

Common action of alcohol (alcoholysis) and water (hydrolysis) can finally lead to conversion of salt to oxosalts or metal oxide, depending on nature of cation and anion of salts and kind of alcohol. Thus, interaction of ZrCl₄ with EtOH or SiCl₄ with t-BuOH, for example, results in the formation of MO₃₂H₂O. At the same time interaction of Zn(OAc)₂ with alcohol results in formation of zincoxoacetate.

The use as precursors of metal salts alone or, in certain embodiments, in combination with metal alkoxides, allows for the formation of coatings not possible by any other known methods and provides a pathway to fully exploit the processing and protection needed in nanostructured conductive coatings to function in electronic devices. Metal alkoxides can be made from many of the elements in the periodic table. However, for metal alkoxides, not all metal elements are possible, not all combinations are possible, and some are too expensive for commercial use. Additionally, it is often advantageous to form coatings which comprise a combination of metal oxides which are not possible by the metal alkoxide chemistries. Therefore, in certain embodiments of
the present invention, metal salts are employed to reach the desirable composite formulation in an economically attractive and technically feasible process. The use of metal salts to form a wide variety of metal oxide conductive composites may be accomplished by use of a mixture of metal salts or a mixture of metal salts in combination with metal alkoxides to form the co-continuous phase with the conductive network.

One advantage of the metal salt-based coating solutions according to certain embodiments of this invention is that metal salt-based solutions are indefinitely stable in solid or in solution, whereas metal alkoxides degrade or decompose rapidly with exposure to air and moisture. The use of metal oxides as a precursor to make the coating solutions greatly reduces losses during the manufacturing process and reduces the need for filtration and other processing equipment typically employed during coating with a far less stable metal alkoxide solution.

Metal salts are also generally significantly less expensive precursors of metal oxides, making the final coated product less costly. Also, a film formed from a metal salt solution is denser than a film from a metal alkoxide solution of the same weight percentage and has a much lower degree of shrinking during the final cure process. This difference is due to the greater porosity of films formed from metal alkoxides. The higher density accomplished through embodiments of the present invention eliminates film cracking and residual stresses due to CTE mismatches between coating and substrate during elevated temperature curing or dehydration.

Addition of a metal oxosalt coating to a CNT network according to certain embodiments preferably provides multiple functions, including, but not limited to, the improvement of one or multiple of the following properties of the CNT layer compared to the same coating without a metal oxosalt binder: heat stability, UV stability, electromagnetic radiation stability, humidity stability, chemical stability, haze, diffuse light transmittance, mechanical bonding to a substrate, electrical contact with a substrate, work function control, type of charge carrier, mechanical strength, abrasion resistance, sheet resistance, broad spectrum transparency, specific wavelength transparency, refractive index matching.

Preferably, salts are in the form of MOHxLy, where x+y is 1-5, OH is hydroxide. Preferably, M is selected from, but not limited to, Al, Zn, Ti, Si, Sn, Bi, In, Pb, Cr, Nb, Ta, V, Sc,Ln, Mn, Mo, W, Co, Ni, Cu, Ge, Ga, Zr, Mg , Ba , Fe, etc. In certain embodiments, L is selected from, but not limited to, chloride, fluoride, iodide,
bromide, acetate, propionate, carboxylate, organic anions, and mixtures thereof.
Combinations of metal oxides with metal oxosalts are advantageous and preferred for some applications. CNT-metal oxosalts coatings preferably maintain surface conductivity, have improved abrasion resistance, and reduce or eliminate UV and thermally induced changes in sheet resistance.

In certain embodiments, binders, top coats, anti-reflective coatings, film stabilizers, or combinations thereof are deposited onto a class of materials known as porous metallic films which include CNT. These films show approximately linear IV characteristics with little to no hysteresis. These films are generally less than about 1 micron thick, and preferably less than about 100 nm thick, and more preferably less than about 50 nm thick. The films are comprised of one or more materials, including but not limited to single walled carbon nanotubes, double walled carbon nanotubes, multiwalled carbon nanotubes, graphite, graphene flakes and sheets, amorphous carbon, gold nanowires, silver nanowires, nickel nanowires, platinum nanowires, InP nanowires, Si nanowires, GaN nanowires, nanoporous gold, nanoporous silver, nanoporous platinum, nanoporous palladium, nanoporous copper, nanoporous nickel, gold, silver, platinum, palladium, copper, nickel, iron, cobalt, yttrium, indium tin oxide, antimony tin oxide, aluminum doped zinc oxide, indium zinc oxide, transparent conductive oxides, semimetals, Alkalis, Alkaline earths, Lanthanides, Actinides, Transition metals, Poor metals, Metalloids, alloys thereof, and combinations thereof. These films contain pores representing about 1%-99.9% void space by volume, preferably about 10% to 75% void space, and more preferably about 30% to 60% void space. The diameters of the pores range from preferably about one micron to about 1 angstrom, and more preferably from about 200 nm to about 1 nm to minimize light scattering.

Fabrication of coatings by these methods includes preparation of a salt precursor in solution of alcohol with or without adding of water in a definite ratio. Any alcohols that are volatile and can dissolve appropriate salt are suitable. Isopropanol and ethanol are preferred solvents. In certain embodiments, a small amount of water or water solutions of acids such as HCl or acetic acid are added to the solution, in the case of using anhydrous salts. Preferably, the water or water acid solution is added in a defined ratio. The ratio is preferably from \( \text{M}:\text{H}_2\theta = 0.2-5.0 \), and more preferably from \( \text{M}:\text{H}_2\theta = 0.2-0.4 \). In certain embodiments, this ratio depends on the kind of substrate. For example, PET substrates have lower wettability than glass, and therefore metal oxosalts solutions deposited on substrates with low wettability preferably have limited water
content to avoid dewetting. Alternatively, a surfactant is added in certain embodiments to improve the wettability of the metal oxosalt solution on substrates with low wettability. In one embodiment, carbon nanotubes are used as a surfactant in the metal oxosalt solution.

Refluxing the metal salt in solvent is preferred. Refluxing the metal salt for several hours is most preferred for increasing the rate of the process of hydrolysis and creation of M-O-M networks. The time of refluxing is preferably from 3-15 hours and more preferably from 3 to 5 hours. The concentration of salts solution is preferably between 1% by weight and about 25% by weight, and more preferably about 6% to 15% by weight depending on the composition. Most preferred salt metals are chlorides, and acetates of metals of 1, 2, 3 b group of Periodic Table. Other preferred metal salts have the form MLx, where M is Al, Zn, Ti, Si, Sn, Bi, In, Pb, Cr, Nb, Ta, V, Sc, Ln, Mn, Mo, W, Co, Ni, Cu, Ge, Ga, Zr, Mg, Ba, or Fe. Preferably, L is chloride, fluoride, iodide, bromide, acetate, propionate, carboxylate, organic anions, and mixtures thereof, and x is the valency of the metal.

In one embodiment the metal salts solution is combined with polymers such as polyethylene, polypropylene, polycarbonate, polyethylene terephthalate, polyvinylene fluoride, Nafion, polyactic acid, polyvinyl acetate (PVA), guar gum, cellulose gum, polyacrylamide, starch, polystyrene sulfonic acid, water soluble polymers, alcohol soluble polymers, and combinations thereof. Carbon nanotubes and nanowires are considered polymers, and thus carbon nanotubes or nanowires may be added to the film former and be co-deposited with the metal salt in certain embodiments. The polymers and metal salts are preferably co-deposited onto CNT film to improve, for example, durability, flexibility, bonding to substrate, refractive index and combinations thereof. The ratio of polymer to salt is preferably between about 1:100 and 100:1 by weight and more preferably 1:10 and 10:1 by weight.

In certain embodiments, metal salt solution is deposited onto CNT coated substrates via any conventional wet-coating method. Such methods include spin coating, dip coating, kiss coating, knife casting, gravure or slot die. Evaporation of the carrier solvents result in uniform coating of the substrate, which is preferable. The substrate may have on the surface one or more of the porous metallic films according to certain embodiments. Preferably, CNT films on glass or plastic substrates are dip coated in salt metal solution and withdrawn from the solution at a rate between 0.05 and 1.200 inches per minute, and more preferably between 1 and 100 inches per minute. In one
preferred embodiment, several separate coatings of a single type or composition of salt metal are applied. In one embodiment, the CNT film is coated with salt metal solution, InCl$_3$ for example, and is allowed to dry in air for about 5 seconds to several hours, depending on desired drying conditions. The sample is then preferably re-coated with the same solution, resulting in multilayer coatings or multi interpenetrated coatings to form a composite layer.

In some embodiments, the number of additional coatings can range from no additional coatings to about ten additional coatings. In another preferred embodiment, the CNT films is coated with one metal salt solution (e.g. indium chloride), and is then preferably allowed to dry, after which it is preferably coated with a different salt metal solution (e.g. tin chloride). Preferably, a sample is coated with several different types of salt metal solutions according to certain embodiments. In a preferred embodiment, the CNT film can be coated with different solution composition (e.g. metal alkoxide solution) and, after drying, preferably coated with salt metal solution leading to multilayer coating. In another preferred embodiment, mixtures of metal salts in solution are employed as a film former, for example indium chloride and tin chloride. This embodiment can be combined with previous embodiments, so that preferably several layers of mixed and single metal salt solution as well as combinations of metal alkoxide and metal salt solution are deposited onto CNT films.

The drying process occurs preferably at between about 100 degrees and about 600 degrees Celsius, and more preferably at between about 100 and 180 deg C. The time for drying is preferably between about 30 minutes and about 48 hours, and more preferably between about one hour and about 6 hours. The preferred atmosphere for baking or dehydration depends on particular composition and may be air or inert gas, according to certain embodiments.

After dehydration, it is preferred that CNT-oxosalt composite retain surface conductivity. While not bound to theory, it is thought that such a coating partially fills the pores in the CNT network and binds the nanotubes together and can lead to cross links within the binder and between the binder and the functional groups of the CNT. Preferably, the films according to such embodiments are not substantially thicker than a nanotube network, since surface conductivity remains after multiple coatings. The preferred thickness of the CNT-oxosalt composite is less than 1 micron. A further preferred thickness of the CNT-oxosalt composite is less than about 500 nm. A most preferred thickness of CNT oxosalt composite is between about 150 nm and 15 nm.
Additionally, as more coatings or higher concentrations of coatings are applied according to certain embodiments, the CNT layer will preferably become covered or encapsulated, whereby the layer is preferably electrically isolated from the surface of the composite layer. Such embodiments provide utility to applications in which electrodes are needed to generate an electrical field but not conduct an electrical current.

After dehydration or drying of a CNT-oxosalt composite according to certain embodiments, the sequential addition of polymer binders, coatings or film is beneficial to improve specific properties of the CNT-oxosalt composite such as: conductivity; haze; transparency; reflectivity; clarity; color neutrality; index of refraction; changes in sheet resistance due to humidity, UV, or heat; abrasion resistance; flexibility; adhesion; chemical resistance; and combinations thereof.

The range of polymers that can be added sequentially according to certain embodiments of this invention is substantially broad and includes all classes or polymers listed above, conjugated polymers, ceramic polymers, ceramic hybrid polymers, polyethylene, polypropylene, polyvinyl chloride, styrenes, polyurethane, polyimide, polycarbonate, polyethylene terephthalate, cellulose, gelatine, chitin, polypeptides, polysaccharides, polynucleotides, and mixtures thereof. In one embodiment, the plastics may be thermosets, thermoplastics, elastomers, conducting polymers, fully or partially halogenated polymers, acidic polymers, ionic polymers and combinations thereof.

Other additives may preferably be included in the polymer or added sequentially, according to various embodiments, to improve the functional properties of the CNT layer or coating. In a preferred embodiment, the added polymer coating is polystryrene sulfonic acid. In another preferred embodiment, the added polymer is PTFE (Teflon). In another preferred embodiment, the added polymer is Nafion. In another preferred embodiment, the added polymer is PVDF. In a more preferred embodiment, the CNT-metal oxosalt-polymer composite retains surface conductivity.

The concentration of the oxosalt is a factor in how well the oxosalt protects CNT or improves CNT properties in certain embodiments. In some embodiments, after deposition and curing, CNTs coated with low concentration oxosalts experience a small increase in sheet resistance, whereas CNTs coated with high concentration oxosalts experience a decrease in sheet resistance. In preferred embodiments, any amount of oxosalt deposited and cured onto the CNT will cause a smaller sheet resistance change than a bare CNT film cured under the same test conditions. This effect depends on the
metal, anion, degree of hydrolysis, solvent, wet coating thickness, deposition method, and curing conditions, among others. For example, a thick wet coating of low concentration oxosalts will protect better than a thin coating of low concentration oxosalts.

In a preferred embodiment, the addition of a coating or coatings comprising one or more oxosalts to a CNT film lowers the sheet resistance of the CNT layer. In one embodiment, the addition of a coating or coatings comprising one or more oxosalts to a CNT film lowers the sheet resistance of the CNT layer between about 25% and 5% depending on concentration of solution and kind of substrate. In another embodiment, the addition of a coating or coatings comprising one or more oxosalts to a CNT film lowers the sheet resistance of the CNT layer between about 10% and 5%. In another embodiment, the addition of a coating or coatings comprising one or more oxosalts to CNT films changes the sheet resistance of CNT layer about less than 5%. In another embodiment, the addition of a coating or coating comprising one or more oxosalts to CNT film followed by the addition of a coating or coating comprising polymers does not change the sheet resistance of the CNT layer. In another embodiment, the addition of a coating or coating comprising one or more oxosalts to CNT film followed by the addition of a coating or coating comprising polymers lowers the sheet resistance of the bare CNT film.

Without wishing to be bound by theory, the decrease in CNT sheet resistance upon deposition of metal alkoxides or metal oxosalts followed by curing of the metal alkoxides or metal oxosalts is thought to be due to consolidation or "compression" of the CNT by metal alkoxide or metal oxosalt binder. It is well known by those skilled in the art that gels formed from metal alkoxides densify upon drying and further density upon curing. Metal alkoxide and metal oxosalt compositions deposited onto CNT films according to certain embodiments lead to coverage of the CNT network with an undensified coating. Upon heating or curing in certain embodiments, the interpenetrated coating loses volume and causes the overlapping or crossing nanotubes to become closer together. These junctions are thought to be the most resistive part of the CNT film, and increasing nanotube-nanotube contact increases inter-tube conductivity and results in decreased electrical resistance through the net of CNT.

In a preferred embodiment, the addition of a coating or coatings comprising one or more metal oxosalts to a CNT film causes the sheet resistance of the composite to remain stable over an extended period of time when exposed to typical environmental conditions or manufacturing process conditions. In a further preferred embodiment, the
addition of a coating or coatings comprising one or more metal oxosalt to a CNT film causes the sheet resistance of the composite to remain stable at room temperature, room lighting, and room humidity over an extended period of time. In a further preferred embodiment, the addition of a coating or coatings comprising one or more metal oxosalts to a CNT film causes the sheet resistance of the composite to remain stable at elevated temperature and outdoor lighting. In a further preferred embodiment, the addition of a coating or coatings comprising one or more metal oxosalts to a CNT film causes the sheet resistance of the composite to increase less than 10% at room temperature and room lighting over a period of about 1000 hours. In a further preferred embodiment, the addition of a coating or coatings comprising one or more metal oxosalts to a CNT film causes the sheet resistance of the composite to increase less than 30% at 100 deg C for over 500 hours. In a further preferred embodiment, the addition of a coating or coatings comprising one or more metal oxosalts to a CNT film causes the sheet resistance of the composite to increase less than 10% at 100 deg C for 500 hours.

In a further preferred embodiment, the addition of a coating or coatings comprising one or more metal oxosalts to a CNT film causes the sheet resistance of the composite to increase less than 35% at under UV exposure for 260 hours. In another preferred embodiment, the addition of a coating or coatings comprising one or more metal oxosalts to a CNT film causes the sheet resistance of the composite to increase less than 5% at 100 deg C and under UV exposure for 500 hours.

In a preferred embodiment, the addition of a polymer coating or coatings to a CNT-metal oxosalts composite forms a CNT-metal oxosalts-polymer composite with a total light transmittance about equal to the CNT film without any added films. In another preferred embodiment, the addition of a polymer coating or coatings to a CNT-metal oxosalts composite forms a composite with a total light transmittance up to about 5% absolute transmittance greater than the CNT film without any added films. In another embodiment, the addition of a polymer coating or coatings to a CNT-metal oxosalts composite forms a composite with a total light transmittance up to about 5% absolute transmittance less than the CNT film without any added films.

In one embodiment, specific metal alkoxide precursors are used to form a coating that comprises a metal oxide with specific protective properties. For example, it is known to those skilled in the art that Cerium oxide (CeO₂) is a valuable additive to borosilicate glass to improve the solar radiation resistance of the glass in space (LEO, MEO, GEO), to reduce or eliminate coloration of the glass during solar radiation, and to
reduce or eliminate the radiation damage of a device or solar cell that is covered by the CeO$_2$ doped glass. The use of a thin film that comprises conductive nanotubes and metal oxides comprising cerium oxide presents a significant advantage over current cover glass in terms of weight, thickness, mechanical flexibility, surface conductivity, and static charge dissipation. In certain embodiments, cerium alkoxides are mixed with other metal alkoxides to coat CNT films as described above. The preferred weight percentage of Ce is between about 1% and about 50%, depending on the level of exposed radiation and the desired lifetime of the coating or space craft. The Ce alkoxide is optionally blended with other metal alkoxides or is deposited sequentially with other metal alkoxides to form an interpenetrated composite or a layered composite, respectively.

The following examples illustrate embodiments of the invention, but should not be viewed as limiting the scope of the invention.

Examples

Metal salt solution of InCB with suitable solvent for mono or multilayer coating was prepared.

A 15% solution of InCl$_3$ was prepared in isopropanol (IPA). 4.73 g of InCl$_3$·4H$_2$O was dissolved in 25.3 g of IPA and refluxed for 4 hours. This solution was cooled and used without further processing under standard atmospheric conditions.

Another example is the preparation of 3.7% of ZnCl$_2$ solution in IPA. 2.3 g of ZnCl$_2$ was dissolved in 61.1 g of IPA. 5 drops of concentrated HCl was added and the solution was sonicated in an ultrasonic bath for 2 minutes. The ZnCl$_2$ solution was refluxed for 10 hours before using.

For purposes of investigating influences of salt precursors and subsequent oxosalt only on CNT transparent conductive films, a separate set of experiments was conducted to evaluate the influences of solvent and water acid mixture used on optoelectronic properties of CNT films. The solution concentration was optimized with coating process conditions to achieve an optimum indium oxochloride thickness by dip coating—approximately 15% by weight. This concentration provided both good optical clarity and good protection of the CNT film.

For purposes of investigating influences of salt precursors and subsequent oxosalt only on CNT electrodes, a separate set of experiments was conducted to evaluate the influences of solvent and water acid mixture used on optoelectronic properties of CNT films. Solution concentration was optimized with coating process conditions to
achieve a target metal oxosalt thickness by dip coating —approximately 0.25-25% by weight, depending on the particular composition and route of decomposition. For example, dip coated solutions typically required higher weight percentages on metal oxosalt solution between about 2% to about 25% for dip coating, and between about 0.25% and about and about 10% for slot die or draw-down coatings.

Glass and PET slides were then prepared by spray coating CNT to a surface resistance of 300-500 Ohms/sq, with parallel silver electrodes at opposite ends of the slides. Slides were baked at 350 deg C for glass and 130 deg C for PET to stabilize painted silver electrodes prior to deposition of the CNT layer. The sheet resistance sprayed values are referred to as Rsprayed. Coatings were prepared by dipping CNT coated on both kinds of slides into salt metal precursor solution.

The other method of deposition was the drawdown method. In this case the concentration of starting solution is preferably much lower in comparison with the concentration used in the deep coating method for forming a coating of the same thickness.

Thus coated glass and PET substrates were first pre-dried under ambient conditions followed by a thermal treatment for 2.5 hours at 100-130 deg C and stored in a moisture-free environmental until tested. These sheet resistance values are referred to as Rstart.

Influence of heat (for example, 100 deg C at static humidity) on opto-electronic properties of oxosalt protected CNT films was measured as a function of time and compared with CNT coatings without oxosalt layer.

**Environmental Stabilization by Monolithic Salt Metal Coatings**

Single layer oxosalt coatings were first deposited over the surface of 300 Ohms/sq CNT films using a dip coating method. The resultant composition was then tested under heat. Coating compositions evaluated include a single layer oxosalt protective layer on CNT in the form of:

a. Glass/CNT/InOxClY
b. PET/CNT/InOxClY

Unprotected CNT films demonstrated a rapid increase in surface resistance over time with heating at 100 deg C, resulting in approximately 30-80% increase in Rs at the end of the test depending on the kind of substrate. Oxosalt suppressed Rs loss under heat. Oxosalt coating minimized heat related degradation of CNT coatings for applications that require elevated temperature stability.
Environmental Stabilization by Hybrid Salt Metal Coatings

Based on data generated from single-layer oxosalt coating test, improved performance could be derived from a bi-component system, based on In and Sn chlorides. More specifically, this evaluation consisted of the following hybrid structure:

a. Glass /CNT/InOxCly/SnOx Cl\textsubscript{y}

b. PET/ CNT/InOxCly/SnOx Cl\textsubscript{y}

Thermal stability was improved by these hybrid coatings where InCl\textsubscript{3} and SnCl\textsubscript{4} are mixed in one solution (Figures 3 and 4).

Environmental Stabilization by Hybrid Metal Alkoxides, Salt Metal Coatings

Based on at least data generated from single-layer salt-metal coating tests, improved performance can be derived from combinations of layers deposited from metal alkoxides and salt metal solutions (Figure 5 and 6). An example of such a combination includes a Zn (OAc)\textsubscript{2} or ZnCl\textsubscript{2} solution in combination with Ti and Al alkoxides solution for formation of a multilayer coating.

Before deposition, the solution is refluxed for several hours, which leads to partial hydrolysis of salts and formation of oxocompounds in solution. The film solution treated in this way, in alcohol, comprising one or more salts is deposited onto a carbon nanotube (CNT) layer or film. Upon deposition, the solvent and water evaporate, partially forming the films of oxosalts.

Other embodiments and uses of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. All references cited herein, including all publications, U.S. and foreign patents and patent applications, including U.S. Provisional Application No. 60/876,165 entitled "Protective Coatings for Porous Conductive Films and Coatings," to which the instant application claims priority, are specifically and entirely incorporated by reference. The term "comprising" as used throughout this application includes the more limiting terms and phrases "consisting essentially of" and "consisting." It is intended that the specification and examples be considered exemplary only with the true scope and spirit of the invention indicated by the following claims.
Claims

1. A composite comprising an electrical network and a network of amorphous metal oxide, as an insular, wherein the composite is electrically stable, and wherein the metal oxide is formed from a precursor selected from the group consisting of an oxo-alkokso-salt, a metal oxosalt, and combinations thereof.

2. The composite of claim 1, wherein surface resistance of the composite undergoes a less than 25%, less than 20%, less than 15%, less than 10%, or less than 5% change, or no detectable or significant change upon exposure to temperatures of 80°C or greater, electromagnetic radiation, UV radiation, a relative humidity of 15% or greater, physical stress, chemical stress, mechanical stress.

3. The composite of claim 1, wherein the composite has a thickness, a length and a width, wherein the length to thickness ratio is 100,000 or greater, wherein the width to thickness ratio is greater than 100,000, or combinations thereof.

4. The composite of claim 3, wherein the thickness of the composite is less than 500 run, less than 200 nm, or less than 100 nm.

5. The composite of claim 1, wherein the electrical network is comprised of single walled carbon nanotubes, double walled carbon nanotubes, multiwalled carbon nanotubes, graphite, graphene flakes and sheets, amorphous carbon, gold nanowires, silver nanowires, nickel nanowires, platinum nanowires, InP nanowires, Si nanowires, GaN nanowires, nanoporous gold, nanoporous silver, nanoporous platinum, nanoporous palladium, nanoporous copper, nanoporous nickel, gold, silver, platinum, palladium, copper, nickel, iron, cobalt, yttrium, indium tin oxide, antimony tin oxide, aluminum doped zinc oxide, indium zinc oxide, transparent conductive oxides, semi-metals, alkalis, alkaline earths, lanthanides, actinides, transition metals, poor metals, metalloids, alloys of any of the foregoing, or combinations thereof.

6. The composite of claim 5, wherein the carbon nanotubes of the composite are substantially uniformly distributed, substantially aligned, substantially disentangled, or combinations thereof.

7. The composite of claim 1, wherein the carbon nanotubes of the composite have aspect ratios of 1-100, 100-1000 or greater than 1000.
8. The composite of claim 1, wherein the composite has an optical transparency of greater than 60%, greater than 70%, greater than 80%, greater than 90%, greater than 95% or about 100%.

9. The composite of claim 1, wherein the composite has a surface resistance of less than $10^6 \, \Omega$/square, less than $10^5 \, \Omega$/square cm, less than $10^4 \, \Omega$/square cm, less than $10^3 \, \Omega$/square D, less than $10^2 \, \Omega$/square D, or less than $10 \, \Omega$/square cm.

10. The composite of claim 9, wherein the precursor comprises a metal salt containing Al, Zn, Ti, Si, Sn, Bi, In, Pb, Cr, Nb, Ta, V, Sc, Ln, Mn, Mo, W, Co, Ni, Cu, Ge, Ga, Zr, Mg, Ba, Fe, chloride, fluoride, iodide, bromide, acetate, propionate, carboxylate, organic anions or combinations thereof.

11. The composite of claim 1, wherein the network of carbon nanotubes and the network of metal oxide are continuous and porous, and wherein the continuous and porous network of carbon nanotubes interpenetrates with the continuous and porous network of metal oxide to form a continuous and porous composite network.

12. The composite of claim 1, wherein the composite comprises a substrate selected from the group consisting of polymer film, glass substrate, polymer, polyester, polycarbonate, polyolefin, polyurethane, acrylate, epoxy, fluorocarbon elastomer, plastic, thermoplastic, polyethylene terephthalate, polyethylene naphthalate, and combinations thereof.

13. The composite of claim 1, wherein the composite comprises one or more layers containing the amorphous metal oxide.

14. The composite of claim 13, wherein the one or more layers containing the amorphous metal oxide have a surface resistance of greater than $10^7 \, \Omega$/square D, greater than $10^6 \, \Omega$/square cm, greater than, greater than $10^5 \, \Omega$/square cm, or greater than $10^2 \, \Omega$/square cm.

15. The composite of claim 13, wherein the composite comprises a separate layer containing the carbon nanotubes, and wherein the surface resistance of the one or more layers containing the amorphous metal oxide to surface resistance of the layer containing the carbon nanotubes ratio is greater than 10, greater than $10^2$, greater than $10^5$, or greater than $10^7$.

16. The composite of claim 1, wherein the composite further comprises a polymer.

17. The composite of claim 16, wherein the polymer is selected from a group consisting of polyester, polyurethane, polyolefin, fluoroplastic, fluoroelastomer,
thermoplastic elastomer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, polyvinylalkyl vinyl ether, a melamine/acrylic copolymer, UV curable epoxy, a copolymer or polymer mixture, and combinations thereof.

18. A method of forming an electrically conductive and transparent film comprising:
   providing an electrically conductive network of carbon nanotubes; and
   depositing a metal salt solution comprising an alcohol and an acid onto the network, wherein the metal salt undergoes hydrolysis to be converted to a metal oxide.

19. The method of claim 18, further comprising air drying the film.

20. The method of claim 18, wherein the depositing of the metal salt solution comprises dip coating the network into the solution.

21. The method of claim 18, further comprising heating the film at a temperature of between approximately 60 and 200 degrees Celsius.

22. The method of claim 18, wherein the heating is performed for more than 15 minutes, more than 30 minutes, more than 1 hour, more than 1.5 hours, more than 2 hours, more than 2.25 hours, more than 2.5 hours.

23. The method of claim 18, further comprising depositing a polymeric coating on the composite.

24. The method of claim 23, wherein the polymeric coating comprises polyester, polyurethane, polyolefin, fluoroelastomer, fluoroplastic, thermoplastic elastomer, polyvinylidene fluoride, polyvinyl fluoride, polychlorotrifluoroethylene, polyvinylalkyl vinyl ether, a melamine/acrylic copolymer, UV curable epoxy, a copolymer or polymer mixture, or combinations thereof.

25. The method of claim 23, wherein the polymeric coating is adhesive.

26. The method of claim 23, wherein the polymeric coating prevents degradation of the composite due to mechanical or physical stress.

27. The method of claim 23, wherein the polymeric coating has an index of refraction which matches adjacent layers.

28. The method of claim 18, wherein the depositing of the metal salt solution is repeated after the air drying.

29. The method of claim 18, wherein surface resistance of the film undergoes a less than 25%, less than 20%, less than 15%, less than 10%, less than 5% change or no detectable or significant change upon exposure to temperatures of 80°C or greater,
emagnetic radiation, UV radiation for more than 100 hours, a relative humidity of 15% or greater, physical stress, chemical stress, mechanical stress.

30. The method of claim 29, wherein the metal salt solution comprises wherein the precursor comprises a metal salt containing Al, Zn, Ti, Si, Sn, Bi, In, Pb, Cr, Nb, Ta, V, Sc, Ln, Mn, Mo, W, Co, Ni, Cu, Ge, Ga, Zr, Mg, Ba, Fe, chloride, fluoride, iodide, bromide, acetate, propionate, carboxylate, organic anions or combinations thereof.

31. A composite formed by the method of claim 18.

32. A method of patterning an electrically conductive and transparent coating comprising:
   - depositing a layer of carbon nanotubes onto a film;
   - selectively depositing a metal salt solution onto a portion of the layer of carbon nanotubes;
   - heating the film comprising the carbon nanotubes and the metal salt solution; and
   - removing a portion of the carbon nanotubes onto which the metal salt solution was not deposited to form a pattern.
Figure 1. 100 deg heat stability of CNT/oxosalts InCl3 composition on glass (1 dip).
Figure 2. 100 deg heat stability of CNT/oxosalt InCl3 composition on PET (1 dip).
Figure 3. 100 deg C Heat Stability of CNT/salt metals composition on glass.
Figure 4. 100 deg C Heat Stability of CNT/salt metals composition on PET.
Figure 5. 100 deg C heat stability of CNT/Multilayer Hybride Salt metal coating where Indium oxosalt is added first, followed by tin oxosalt addition.

Figure 6. 100 deg C Heat Stability of CNT/Metal Alkoxides and Salt metal (Zn(OAc)2) composition on PET. Al and Ti alkoxides were deposited first using one dip, and the Zn acetate was deposited as a second layer.
Figure 7. 100 deg C Heat Stability of CNT/metal alkoxides and metal oxosalt (ZnCl2) composition on PET. Al and Ti alkoxides were deposited first using one dip, and the Zn chloride was deposited as a second layer.