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(54) **METHOD FOR THE ELECTROCHEMICAL DEPOSITION OF CARBON NANOTUBES**

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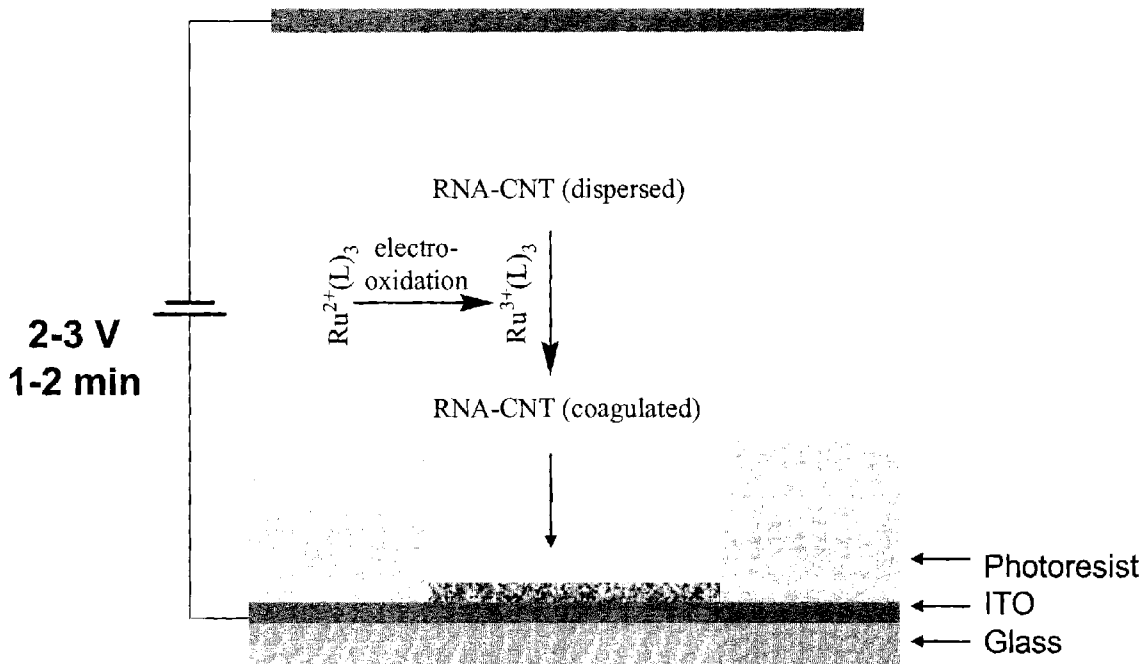
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(57) **ABSTRACT**

This invention relates to the electrochemical deposition of carbon nanotubes ("CNTs") on a substrate using an electrochemical cell. A dispersion of a complex of CNTs and an anionic polymer is neutralized and thereby caused to deposit on the anode plate of the cell.



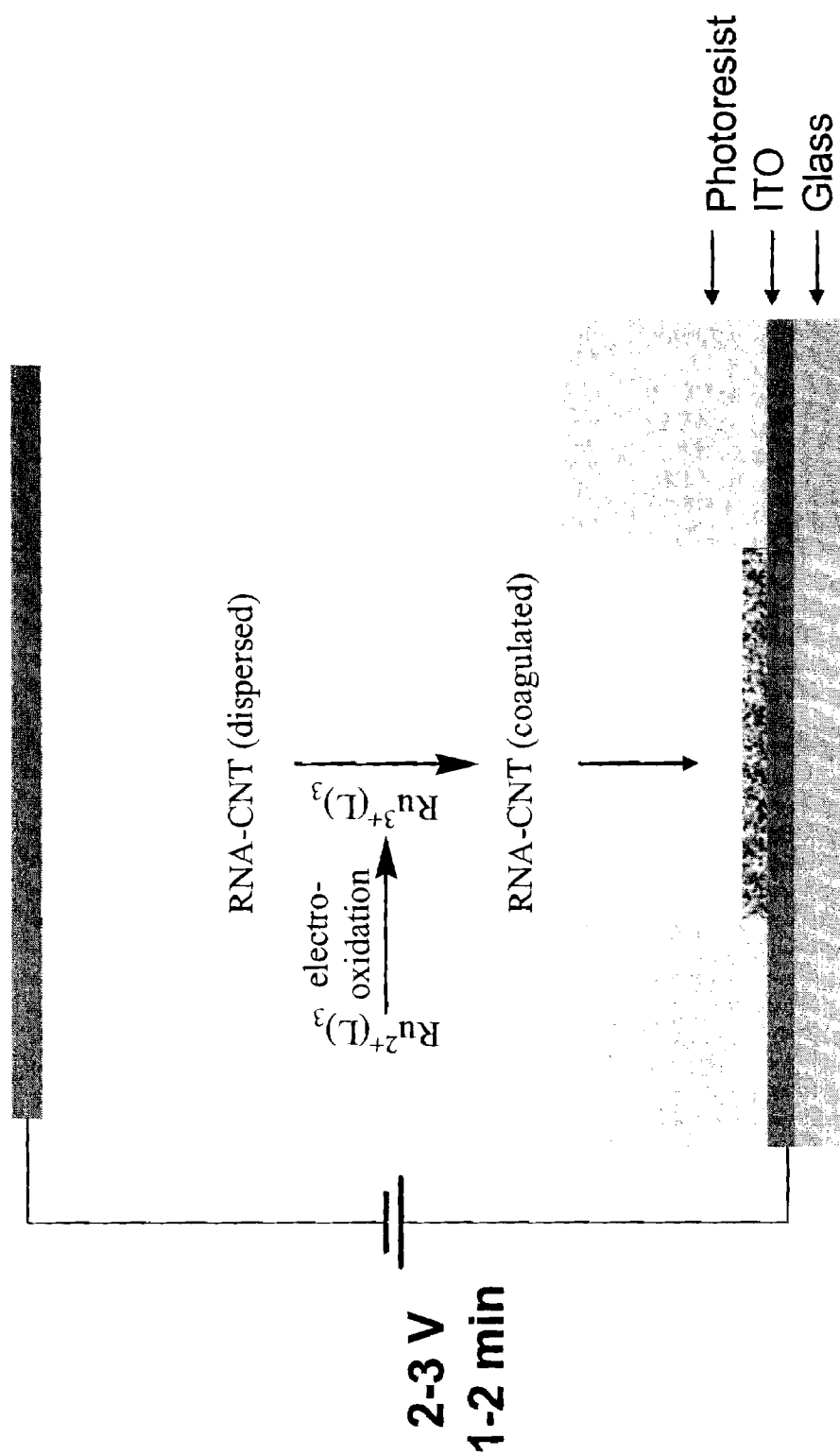


Figure 1

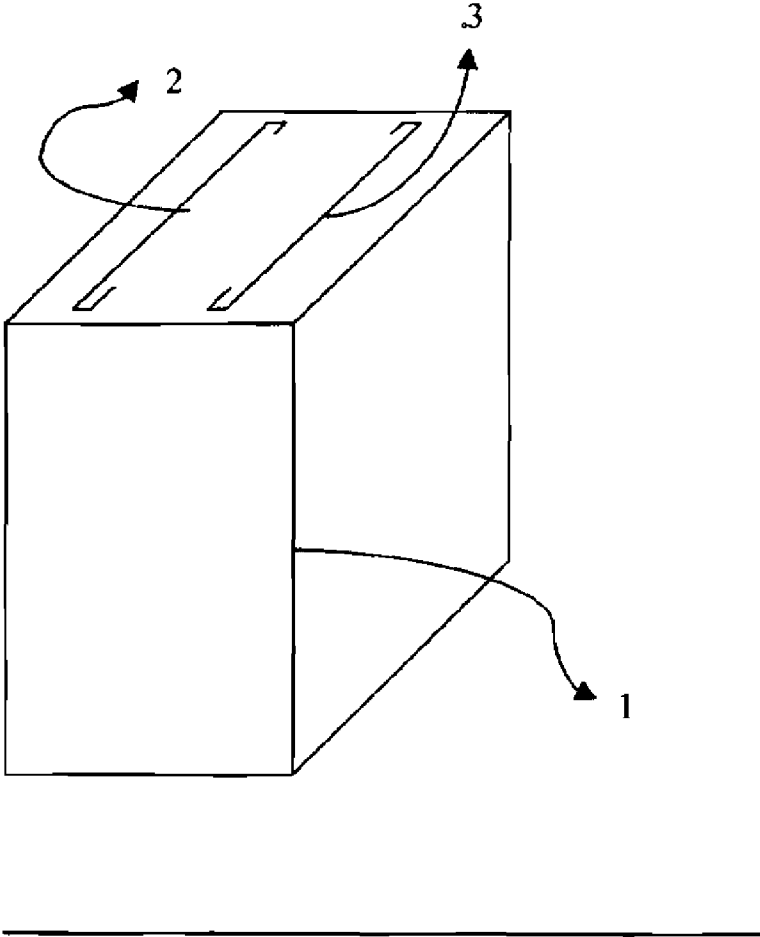


Figure 2

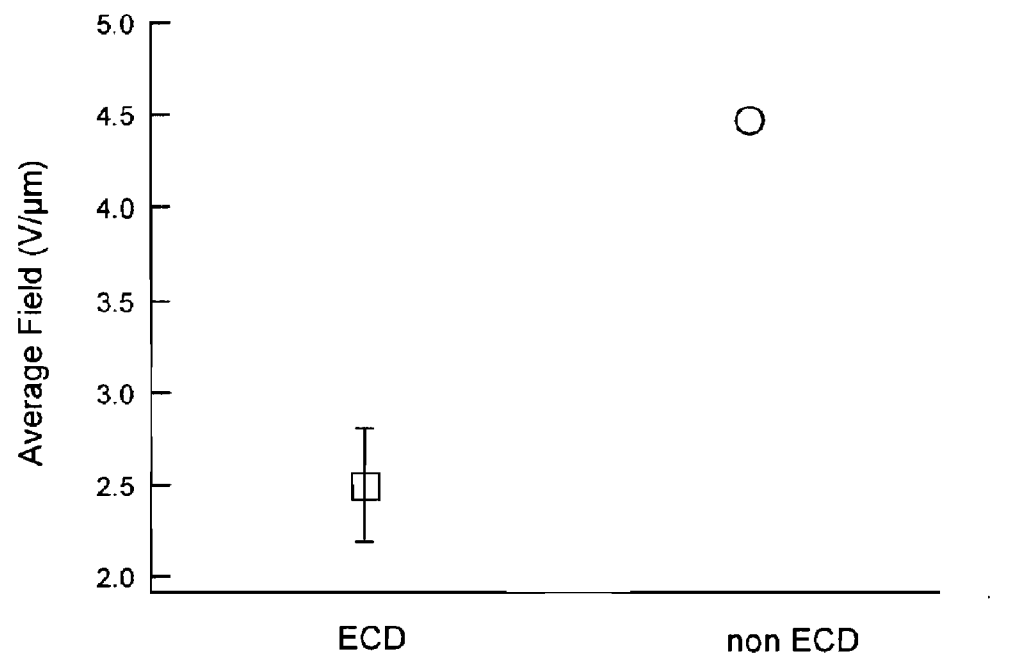


Figure 3

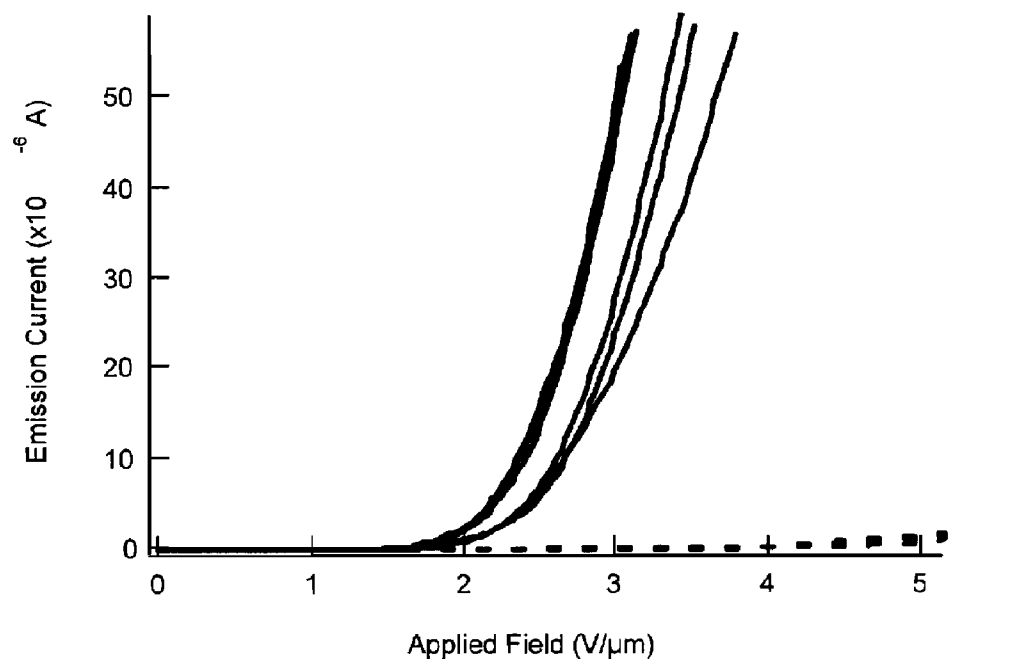


Figure 4

METHOD FOR THE ELECTROCHEMICAL DEPOSITION OF CARBON NANOTUBES

[0001] This application claims priority under 35 U.S.C. §119(e) from, and claims the benefit of, U.S. Provisional Application No. 61/032,505, filed Feb. 29, 2008, which is by this reference incorporated in its entirety as a part hereof for all purposes.

TECHNICAL FIELD

[0002] This invention relates to the electrochemical deposition of carbon nanotubes ("CNTs") on a substrate.

BACKGROUND

[0003] Carbon nanotubes are well known to have unique and useful electrical properties, and are frequently used in the fabrication of the cathode of a field emission device ("FED"). However, adoption of these materials is constrained by their high cost

[0004] US 2006/0063464 describes the deposition of carbon nanotubes by electrochemical methods. A need remains, however, for methods for the electrodeposition of carbon nanotubes that produce electron field emitters with good uniformity and low material consumption, and in which a relatively high emission current is consistently obtained from a relatively low voltage input.

SUMMARY

[0005] One objective of this invention is thus to provide a method for making a uniform CNT film on a substrate such as a conducting substrate with good uniformity and low material consumption. Another objective is to provide a method for making a CNT film that, when used as electron field emitter, consistently produces a relatively high emission current from a relatively low voltage input. A further objective is to provide from this method a CNT film that may be easily patterned for use in electronic applications. The CNT film so patterned may be used, for example, in a cathode assembly that is installed in a field emission device.

[0006] One embodiment of this invention thus provides a method for the deposition of carbon nanotubes by (a) providing an electrochemical cell that comprises a cathode, an anode plate, a first electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate; (b) providing an aqueous electrolyte disposed between the cathode and the anode a dispersion of a complex formed from carbon nanotubes and a first anionic polymer; (c) applying a voltage to the electrochemical cell to deposit the complex on the anode; and (d) removing the anode plate from the electrochemical cell and firing the plate in air.

[0007] In another embodiment, this invention provides a method for the deposition of an electron emitting material on a substrate by (a) providing an electrochemical cell that comprises a cathode, an anode plate, a first electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate; (b) providing an aqueous electrolyte disposed between the cathode and the anode, wherein the electrolyte comprises boric acid and/or a borate compound, and a dispersion of a complex formed from

carbon nanotubes and a first anionic polymer; and (c) applying a voltage to the electrochemical cell to deposit the complex on the anode.

[0008] In a further embodiment, this invention provides a film that includes a substrate and, disposed on the substrate, (a) boric acid and/or a borate compound, and (b) a complex formed from carbon nanotubes and a first anionic polymer. Alternatively, in this embodiment, there may further be disposed on the substrate coagulant residue.

[0009] In yet another embodiment, this invention provides a method for the deposition of an electron emitting material on a substrate, by (a) depositing an electron emitting material on a substrate to prepare an electron field emitter; (b) installing the electron field emitter as the anode plate in an electrochemical cell, wherein the electrochemical cell further comprise a cathode, a first electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate; (c) providing an electrolyte disposed between the cathode and the anode plate that comprises boric acid and/or a borate compound; and (d) applying a voltage to the electrochemical cell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 shows a schematic representation of the mechanism of deposit in one embodiment of the methods of this invention.

[0011] FIG. 2 shows the configuration of an electrochemical cell as used in the examples.

[0012] FIG. 3 shows a plot of the results of Example 1.

[0013] FIG. 4 shows a plot of the results of Example 2.

DETAILED DESCRIPTION

[0014] A CNT film is made by the method of this invention by the deposition of CNTs on a substrate by electrochemical means, and for such purpose the method hereof involves the use of an electrochemical cell. The cell contains a cathode, an anode plate, a first electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate. An aqueous electrolyte is provided to the cell and is disposed between the anode plate and the cathode. Contained in the electrolyte is a dispersion of a complex formed from CNTs and a first anionic polymer, and optionally a coagulant.

[0015] CNTs as used herein are generally about 0.5-2 nm in diameter where the ratio of the length dimension to the narrow dimension, i.e. the aspect ratio, is at least 5. In general, the aspect ratio is between 10 and 2000. CNTs are comprised primarily of carbon atoms, however may be doped with other elements, e.g. metals. The carbon-based nanotubes of the invention can be either multi-walled nanotubes (MWNTs) or single-walled nanotubes (SWNTs). A MWNT, for example, includes several concentric nanotubes each having a different diameter. Thus, the smallest diameter tube is encapsulated by a larger diameter tube, which in turn, is encapsulated by another larger diameter nanotube. A SWNT, on the other hand, includes only one nanotube.

[0016] CNTs may be produced by a variety of methods, and are additionally commercially available. Methods of CNT synthesis include laser vaporization of graphite [A. Thess et al, *Science* 273, 483 (1996)], arc discharge [C. Journet et al, *Nature* 388, 756 (1997)] and HiPCo (high pressure carbon

monoxide) process [P. Nikolaev et al, Chem. Phys. Lett. 313, 91-97 (1999)]. Chemical vapor deposition (CVD) can also be used in producing carbon nanotubes [J. Kong et al, Chem. Phys. Lett. 292, 567-574 (1998); J. Kong et al, Nature 395, 878-879 (1998); A. Cassell et al, J. Phys. Chem. 103, 6484-6492 (1999); H. Dai et al, J. Phys. Chem. 103, 11246-11255 (1999)]. Additionally CNTs may be grown via catalytic processes both in solution and on solid substrates [Yan Li et al, Chem. Mater.; 2001; 13(3); 1008-1014]; (N. Franklin and H. Dai, Adv. Mater. 12, 890 (2000); A. Cassell et al, J. Am. Chem. Soc. 121, 7975-7976 (1999)].

[0017] A major obstacle to the use of CNTs has been the diversity of tube diameters, chiral angles, and aggregation states in nanotube samples obtained from the various preparation methods. Aggregation is particularly problematic because the highly polarizable, smooth-sided fullerene tubes readily form parallel bundles or ropes with a large van der Waals binding energy. This bundling perturbs the electronic structure of the tubes, and it confounds almost all attempts to separate the tubes by size or type or to use them as individual macromolecular species.

[0018] There is thus provided by this invention a method for dispersing a population of bundled carbon nanotubes by contacting the bundled nanotubes with an aqueous solution of an anionic polymer. A complex containing the anionic polymer and the CNTs is thereby formed, but the association between the anionic polymer and the CNTs in the complex is a loose association, is formed essentially by van der Waals bonds or some other non-covalent means, and is not formed through the interaction of specific functionalized groups. The structural integrity of the CNTs is therefore retained, but the complexes they form with the anionic polymers become, when present in the electrolyte, suspended in a dispersion in the electrolyte.

[0019] A variety of anionic polymers may thus be used as dispersants for the purpose of dispersing CNTs in an aqueous solution by facilitating the formation of the polymer/CNT complex, but a preferred polymer for use for such purpose is a nucleic acid, particularly a stabilized solution of nucleic acid molecules. Nucleic acids are very effective in dispersing CNTs by the formation of nanotube-nucleic acid complexes based on non-covalent interactions between the nanotube and the nucleic acid molecule. The method of this invention therefore includes a method for the dispersion of bundled CNTs by contacting the nanotubes with a solution of anionic polymers such as nucleic acid molecules.

[0020] In the following discussion of the use of nucleic acid molecules to form complexes with and thereby disperse CNTs, the following terms and abbreviations are used:

[0021] "cDNA" means complementary DNA

[0022] "PNA" means peptide nucleic acid

[0023] "SEM" means scanning electron microscopy

[0024] "ssDNA" means single stranded DNA

[0025] "tRNA" means transfer RNA

[0026] "CNT" means carbon nanotube

[0027] "MWNT" means multi-walled nanotube

[0028] "SWNT" means single walled nanotube

[0029] "TEM" means transmission electron microscopy

[0030] A "nucleic acid molecule" is defined as a polymer of RNA, DNA, or peptide nucleic acid (PNA) that is single- or double-stranded, optionally containing synthetic, non-natural or altered nucleotide bases. A nucleic acid molecule in the form of a polymer of DNA may be comprised of one or more segments of cDNA, genomic DNA or synthetic DNA.

[0031] The letters "A", "G", "T", "C" when referred to in the context of nucleic acids will mean the purine bases adenine (C₅H₅N₅) and guanine (C₅H₅N₅O) and the pyrimidine bases thymine (C₅H₆N₂O₂) and cytosine (C₄H₅N₃O), respectively.

[0032] The term "peptide nucleic acids" refers to a material having stretches of nucleic acid polymers linked together by peptide linkers.

[0033] A "stabilized solution of nucleic acid molecules" refers to a solution of nucleic acid molecules that are solubilized and in a relaxed secondary conformation.

[0034] A "nanotube-nucleic acid complex" means a composition comprising a carbon nanotube loosely associated with at least one nucleic acid molecule. Typically the association between the nucleic acid and the nanotube is by van der Waals bonds or some other non-covalent means.

[0035] The term "agitation means" refers to a device that facilitate the dispersion of nanotubes and nucleic acids. A typical agitation means is sonication.

[0036] The term "denaturant" refers to substances effective in the denaturation of DNA and other nucleic acid molecules.

[0037] Standard recombinant DNA and molecular biology techniques used here are well known in the art and are described, for example, by Sambrook, Fritsch and Maniatis, *Molecular Cloning: A Laboratory Manual*, Second Edition, Cold Spring Harbor Laboratory Press, Cold Spring Harbor, N.Y. (1989) (hereinafter "Maniatis"); by Silhavy, Bannan and Enquist, *Experiments with Gene Fusions*, Cold Spring Harbor Laboratory Cold Press Spring Harbor, N.Y. (1984); and by Ausubel et al, *Current Protocols in Molecular Biology*, published by Greene Publishing Assoc. and Wiley-Interscience (1987).

[0038] Nucleic acid molecules as used in a method of this invention may be of any type and from any suitable source, and include without limitation DNA, RNA and peptide nucleic acids. The nucleic acid molecules used herein may be generated by synthetic means or may be isolated from nature by protocols known in the art (see, e.g., Sambrook supra). The nucleic acid molecules may be either single stranded or double stranded and may optionally be functionalized at any point with a variety of reactive groups, ligands or agents. Functionalization of nucleic acids is not, however, required for their association with CNTs for the purpose of dispersion, and most of the nucleic acids used herein for dispersion do lack functional groups and are therefore referred to herein as "unfunctionalized".

[0039] Peptide nucleic acids (PNA) are particularly useful herein for dispersion as they possess the double functionality of both nucleic acids and peptides. Methods for the synthesis and use of PNA's are known in the art as discussed, for example, in Antsyovitch, *Peptide nucleic acids: Structure*, Russian Chemical Reviews (2002), 71(1), 71-83.

[0040] Nucleic acid molecules as used herein may have any composition of bases and may even consist of stretches of the same base (poly A or poly T for example) without impairing the ability of the nucleic acid molecule to disperse the bundled CNTs. Preferably the nucleic acid molecules will be less than about 2000 bases where less than 1000 bases is preferred and where from about 5 bases to about 1000 bases is most preferred. Generally the ability of nucleic acids to disperse CNTs appears to be independent of sequence or base composition, however there is some evidence to suggest that the less G-C and T-A base-pairing interactions in a sequence, the higher the dispersion efficiency, and that RNA and vari-

eties thereof is particularly effective in dispersion and is thus preferred herein. Nucleic acid molecules suitable for use herein include without limitation those having the general formula:

- [0041] 1. An wherein n=1-2000;
- [0042] 2. Tn wherein n=1-2000;
- [0043] 3. Cn wherein n=1-2000;
- [0044] 4. Gn wherein n=1-2000;
- [0045] 5. Rn wherein n=1-2000, and wherein R may be either A or G;
- [0046] 6. Yn wherein n=1-2000, and wherein Y may be either C or T;
- [0047] 7. Mn wherein n=1-2000, and wherein M may be either A or C;
- [0048] 8. Kn wherein n=1-2000, and wherein K may be either G or T;
- [0049] 9. Sn wherein n=1-2000, and wherein S may be either C or G;
- [0050] 10. Wn wherein n=1-2000, and wherein W may be either A or T;
- [0051] 11. Hn wherein n=1-2000, and wherein H may be either A or C or T;
- [0052] 12. Bn wherein n=1-2000, and wherein B may be either C or G or T;
- [0053] 13. Vn wherein n=1-2000, and wherein V may be either A or C or G;
- [0054] 14. Dn wherein n=1-2000, and wherein D may be either A or G or T; and
- [0055] 15. Nn wherein n=1-2000, and wherein N may be either A or C or T or G.

[0056] In addition to the combinations listed above, any of these sequences may have one or more deoxyribonucleotides replaced by ribonucleotides (i.e. RNA or RNA/DNA hybrid) or one or more sugar-phosphate linkages replaced by peptide bonds (i.e. PNA or PNA/RNA/DNA hybrid).

[0057] Nucleic acid molecules as used herein may be stabilized in a suitable solution. It is preferred that the nucleic acid molecules be in a relaxed secondary conformation and only loosely associated with each other to allow for the greatest contact by individual strands with the CNTs. Stabilized solutions of nucleic acids are common and well known in the art (see Sambrook, supra) and typically include salts and buffers such as sodium and potassium salts, and TRIS (Tris (2-aminoethyl)amine), HEPES (N-(2-hydroxyethyl)piperazine-N'-(2-ethanesulfonic acid), and MES (2-(N-Morpholino)ethanesulfonic acid). Preferred solvents for stabilized nucleic acid solutions are those that are water miscible where water is most preferred. The process of dispersion may be improved with the optional addition of nucleic acid denaturing substances to the solution. Common denaturants include but are not limited to formamide, urea and guanidine. A non-limiting list of suitable denaturants may be found in Sambrook, supra.

[0058] To prepare a dispersion according to one embodiment of the method hereof, an anionic polymer such as one or more nucleic acid molecules may be contacted with a population of bundled carbon nanotubes. It is preferred, although not required, that contact be made in the presence of an agitation means of some sort. Typically the agitation means employs sonication, but may also include devices that produce high shear mixing of the nucleic acids and CNTs (i.e. homogenization), or any combination thereof. Upon agitation, the CNTs will become dispersed and will form nanotube-nucleic acid complexes comprising at least one nucleic

acid molecule loosely associated with the CNT by hydrogen bonding or some other non-covalent means.

[0059] Temperature during the process of contacting CNTs with a nucleic acid may have an effect on the efficacy of the dispersion. Mixing at room temperature or higher has been seen to give longer dispersion times whereas mixing at temperatures below room temperature (23° C.) has been seen to give more rapid dispersion times, and temperatures of about 4° C. are preferred. The dispersion of CNTs by contact with nucleic acid molecules is also described in US 2004/0132072 and US 2004/0146904, each of which is by this reference incorporated in its entirety as a part hereof for all purposes.

[0060] In addition to the nucleic acid molecules described above, one or more other anionic polymers may be used for the purpose of preparing an aqueous dispersion of CNTs. Examples of other anionic polymers that are suitable for use in the preparation of a dispersion of CNTs include without limitation ionized poly(acrylic acid) ("PAA") or ionized ethylene/(meth)acrylic acid copolymer ("EAA" or "EMAA"), either of which may be neutralized with cations such as Na⁺, K⁺, NH₄⁺ or Cr⁺; styrenic ionomers such as styrene/sodium styrene sulfonate copolymer (PSS) or styrene/sodium styrene methacrylate copolymer; and ionized tetrafluoroethylene/sulfonic acid copolymers such as Nafion™ copolymer (from DuPont) in which the sulfonic acid group in a tetrafluoroethylene/perfluorovinyl ether copolymer may be sodium neutralized. As indicated above with respect to nucleic acid molecules, ultrasonication or other mixing means may be applied to facilitate the dispersion of CNTs in an aqueous solution of one or more of the anionic polymers discussed above.

[0061] In one embodiment, deposition on the anode plate of the cell of the complexes formed from CNTs and molecules of an anionic polymer, as dispersed in the electrolyte solution contained in the cell, will be facilitated by the presence therein of the optional coagulant. The coagulant will neutralize the negative charge on the anionic polymer in the complex. As the population of anionic polymer/CNT complexes has been maintained in dispersion primarily by the repulsion of one negatively charged complex from another (or by the repulsion of positively charged double layers surrounding the complexes), neutralization of those negative charges (or compression of the double layer) by the coagulant will remove the force enabling the population of complexes to remain in dispersion in the electrolyte solution. As the action of the coagulant to neutralize the complexes occurs in close proximity to the anode plate, the complexes (as no longer dispersed) will in varying degrees undergo a transition from solution phase to solid phase, become progressively aggregated and agglomerated (similar to the formation of flocules and flocs), and then be collected and deposited on the surface of the anode plate. In addition to the CNT complexes, the material as deposited on the plate may include coagulant residue.

[0062] When first and second anionic polymers are present in the electrolyte solution, they may be, for example, a first polymer that forms a complex with CNTs, and a second polymer that does not form a complex, or that is more loosely associated with CNTs than the first polymer. The first and second polymers may become deposited on the surface of the anode at the same time, and the first polymer may, for example, be deposited in a matrix of the second polymer. If additional materials, such as conductive or functionalized particles, are needed to enhance the usefulness and performance of the cell anode plate as a component in a field

emission device are present in the electrolyte solution, those materials may be deposited on the anode plate at the same time as the anionic polymer/CNT complexes. FIG. 2 shows a typical example of the type of film formed by such deposition on the anode plate, which film has good uniformity of evenly deposited, well-adhered material all across its surface.

[0063] Coagulants suitable for use herein for the purpose of neutralizing an anionic polymer/CNT complex include inorganic coagulants such as trivalent cations formed from metals including Group VIII/VIIIA metals such as iron, cobalt, ruthenium or osmium. As a trivalent cation can be up to as much as ten times more effective in neutralizing the complex than a divalent cation, a convenient way to provide the coagulant is to supply a divalent cation such as tris(2,2'-bipyridyl)dichloro-ruthenium (II) to the electrolyte solution wherein the 2⁺ cation is oxidized to a 3⁺ valence by the loss of electrons to the anode plate. A schematic representative of this mechanism is shown in FIG. 1. In the case, for example, of the use of a metal cation as the coagulant, coagulant residue will thus be the cation as oxidized by interaction with an anionic polymer/CNT complex.

[0064] In an alternative embodiment, however, a coagulant is not used where the anode plate is formed from a metal such as silver or nickel. In such case, the metal on the plate dissolves in the electrolyte solution, and the charge on an anionic polymer/CNT complex is neutralized by cations formed from metal atoms that have gone into solution from the solid metal from which the plate is formed.

[0065] In a further alternative embodiment, the electrolyte solution may contain, in addition to one or more anionic polymers and the optional coagulant, boric acid and/or a borate compound. Borate compounds suitable for use in the electrolyte solution include, for example, those represented by the structural formula B—(—R³)(—R⁴)(—R⁵), wherein R³, R⁴ and R⁵ may be the same or different, and each independently represents an alkyloxy group, an alkenyloxy group, an aryloxy group, an aralkyloxy group or a halogen atom; and when R⁴ and R⁵ are an alkyloxy group, an alkenyloxy group, an aryloxy group or an aralkyloxy group, R⁴ and R⁵ may be combined to each other to form a cyclic structure together with the boron atom.

[0066] The alkyloxy group represented by R³, R⁴ or R⁵ may have a substituent and specifically, the alkyloxy group is preferably a substituted or unsubstituted, linear or branched alkyloxy group having from 1 to 10 carbon atoms. Examples thereof include methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec-butoxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, 3-methoxypropoxy, 4-chlorobutoxy and 2-diethylaminoethoxy.

[0067] The alkenyloxy group represented by R³, R⁴ or R⁵ may have a substituent and specifically, the alkenyloxy group is preferably a substituted or unsubstituted, linear or branched alkenyloxy group having from 3 to 12 carbon atoms. Examples thereof include a propenyloxy group, a butenyloxy group, a pentyloxy group, a hexenyloxy group, a heptenyloxy group, an octenyloxy group, a dodecenyloxy group and prenyloxy group.

[0068] The aryloxy group represented by R³, R⁴ or R⁵ may have a substituent and specifically, the aryloxy group is a substituted or unsubstituted aryloxy group. Examples thereof include phenoxy, tolyloxy, xylyloxy, 4-ethylphenoxy, 4-butylphenoxy, 4-tert-butylphenoxy, 4-methoxyphenoxy, 4-diethylaminophenoxy, 2-methylphenoxy, 2-methoxyphenoxy, 1-naphthoxy, 2-naphthoxy and 4-methylnaphthoxy.

[0069] The aralkyloxy group represented by R³, R⁴ or R⁵ may have a substituent and specifically, the aralkyloxy group is a substituted or unsubstituted aralkyloxy group. Examples thereof include a benzyloxy group, a phenethyloxy group, a phenylpropyloxy group, a 1-naphthylmethyloxy group, a 2-naphthylmethyloxy group and a 4-methoxybenzyloxy group.

[0070] Specific examples of a borate compound suitable for use herein include a trimethyl borate, a triethyl borate, a tri-n-propyl borate, a triisopropyl borate, a tri-n-butyl borate, a triisobutyl borate, a tri-n-octyl borate, a butyldiethyl borate, an ethyldi(2-phenethyl)borate, a triphenyl borate, a diethyl-4-methoxyphenyl borate, a diethylcyclohexyl borate, trichloroborane, trifluoroborane, diethoxychloroborane, n-butoxydichloroborane, and tris borate(ethylenediaminetetraacetic acid).

[0071] Specific examples of a compound having a cyclic structure containing a boron atom and two oxygen atoms within the ring formed by combining R⁴ and R⁵ to each other include 2-methoxy-1,3,2-dioxaborinane, 2-ethoxy-1,3,2-dioxaborolane, 2-butoxy-1,3,2-dioxaborinane, 2-phenoxy-1,3,2-dioxaborinane, 2-phenoxy-4,4,6-trimethyl-1,3,2-dioxaborinane, 2-naphthoxy-1,3,2-dioxaborinane, 2-methoxy-1,3,2-benzodioxaborole and 2-ethoxy-1,3,2-benzodioxaborin.

[0072] In this embodiment, boric acid and/or a borate compound may be used in the electrolyte solution at a concentration therein in the range of about 0.1 wt % or more, or about 0.5 wt % or more, and yet about 10 wt % or less, or about 5 wt % or less.

[0073] In this embodiment of the method hereof, where boric acid and/or a borate compound is present in the electrolyte solution, the material as deposited on the cell anode plate may thus include, in addition to the CNT complexes, residue of the optional coagulant and/or some of the boric acid and/or borate compound. In such event, a further embodiment of this invention includes a film that is composed of a substrate and, disposed or deposited on the substrate, a complex formed from carbon nanotubes and one or more anionic polymer(s), coagulant residue and/or boric acid and/or a borate compound.

[0074] As the plate that is used as the anode in the electrolytic cell will ultimately be used in the cathode assembly of a field emission device, it is desirable that the plate as used in the cell already be provided with conductive means onto which the CNTs may be deposited. One example of a suitable plate to use for such purpose is a glass plate, such as a soda lime glass plate, that is coated with a conductive material such as indium tin oxide ("ITO"). Alternatively, however, the plate used for such purpose could be a substrate on which conductive materials have first been deposited by thick film paste methods such as described below.

[0075] The method hereof may be used to produce a film in which the deposited material is deposited in a pre-determined pattern. This may be accomplished by patterning the surface of the plate used as the cell anode using conventional photoimaging techniques. Thus a photoresist may be activated through a mask and then developed to provide on the surface of the cell anode a pattern such as an array of circular wells. As the anionic polymer/CNT complexes are aggregated and settle out of solution, they are deposited only in the circular wells, and the photoresist may be removed. This provides a patterned CNT film, with the anode plate serving as a substrate for the film, for use by installation in a field emission device.

[0076] The method hereof is generally performed by operation of the electrochemical cell at lower potential such as less than about 5 volts, or from about 2 to less than about 5 volts, or from about 2 volts to about 3 volts. Thickness of the deposited film is to a large extent directly related to length of deposition time. A deposition time in the range of about 1 to about 10 minutes, or in the range of about 1 to about 2 minutes, may be used. A positive potential is maintained at the cell anode plate relative to the cathode of the cell.

[0077] After completion of the deposition of CNT complex material on the anode plate in the cell, the plate may be removed from the cell, rinsed, dried and installed in such condition in a field emission device for use as part of the cathode assembly therein to provide electron emission. Alternatively, however, before installation in a field emission device, the plate may be baked and/or fired to melt the deposited polymer(s) and utilize them in that form as an adhesive to more securely anchor the CNTs to the surface of the plate, resulting in a CNT-containing film with excellent abrasion resistance. Firing may be performed at a temperature in the range of about 250° C. to about 650° C., or about 350° C. to about 550° C., or about 450° C. to about 525° C., for a period of time in the range of about 5 to about 30 minutes, or about 10 to about 25 minutes, or about 10 to about 20 minutes, in an inert gas such as nitrogen or in air.

[0078] After completion of the deposition of CNT complex material on the anode plate in the cell, the plate may be installed in a field emission device for use as part of the cathode assembly therein to provide electron emission. When a voltage is applied to the CNTs, the anode of the device is bombarded with electrons. The anode of the field emission device is an electrode coated with an electrically conductive layer. When the field emission device is used in a display device where the cathode contains an array of pixels of the thick film paste deposits described above, the FED anode may comprise phosphors to convert incident electrons into light. The substrate of the FED anode would also be selected to be transparent so that the resulting light could be transmitted. From the cathode assembly and FED anode, a sealed unit is constructed in which the cathode assembly and anode are separated by spacers, and there is an evacuated space between the anode and the cathode. This evacuated space is under partial vacuum so that the electrons emitted from the cathode may transit to the anode with only a small number of collisions with gas molecules. Frequently the evacuated space is evacuated to a pressure of less than 10^{-5} Torr.

[0079] Such a field emission device is useful in a variety of electronic applications, e.g. vacuum electronic devices, flat panel computer and television displays, back-light source for LCD displays, emission gate amplifiers, and klystrons and in lighting devices. For example, flat panel displays having a cathode using a field emission electron source, i.e. a field emission material or field emitter, and a phosphor capable of emitting light upon bombardment by electrons emitted by the field emitter have been proposed. Such displays have the potential for providing the visual display advantages of the conventional cathode ray tube and the depth, weight and power consumption advantages of the other flat panel displays. The flat panel displays can be planar or curved. U.S. Pat. Nos. 4,857,799 and 5,015,912 disclose matrix-addressed flat panel displays using micro-tip cathodes constructed of tungsten, molybdenum or silicon. WO 94-15352, WO 94-15350 and WO 94-28571 disclose flat panel displays wherein the cathodes have relatively flat emission surfaces.

These devices are also described in US 2002/0074932, which is by this reference incorporated in its entirety as a part hereof for all purposes.

[0080] In an alternative embodiment of this invention, a field emission device may be made by preparing an electron field emitter by conventional means. Such an electron field emitter would take the form of a substrate on which electron emitting material has been deposited, and would be suitable for use as, or to further prepare, a cathode assembly for use in an FED. The conventional means of preparing the electron field emitter would include, for example, depositing an electron emitting material on a substrate by screen printing a thick film paste. After the electron field emitter has been prepared, it is then installed as the anode plate in an electrolytic cell, as described elsewhere herein. An aqueous electrolyte is provided to the cell and is disposed therein between the cell cathode and the cell anode plate, which is the previously-prepared electron field emitter. Contained in the electrolyte is boric acid and/or a borate compound as described above. A voltage is then applied to the cell, and the cell anode plate (the previously-prepared electron field emitter) is then removed from the cell.

[0081] In the preparation of an electron field emitter to be used in this embodiment as the cell anode plate, there may be, for example, a deposit on a substrate of a thick film paste containing an electron emitting material. The electron emitting material contained in the thick film paste may be any acicular emitting material such as the CNTs described above, other forms of carbon such as carbon fibers, a semiconductor, a metal or mixtures thereof. Carbon fibers useful as an acicular emitting material may be grown from the catalytic decomposition of carbon-containing gases over small metal particles are also useful as acicular carbon, and other examples of acicular carbon are polyacrylonitrile-based (PAN-based) carbon fibers and pitch-based carbon fibers. As used herein, "acicular" means particles with aspect ratios of 10 or more. Typically, glass frit, metallic powder or metallic paint or a mixture thereof is used to attach the electron emitting material to the substrate in the electron field emitter to be used as, or in the preparation of, a cathode assembly.

[0082] In a conventional attachment of an electron emitting material to a substrate, various screen printing-type processes can be used. The means of attachment must withstand and maintain its integrity under the conditions of manufacturing the apparatus into which the field emitting cathode is placed and under the conditions surrounding its use, e.g. typically vacuum conditions and temperatures up to about 450° C. A preferred method is to screen print a paste comprised of the electron emitting material and glass frit, metallic powder or metallic paint or a mixture thereof onto a substrate in the desired pattern and to then fire the dried patterned paste. For a wider variety of applications, e.g. those requiring finer resolution, the preferred process comprises screen printing a paste which further comprises a photoinitiator and a photo-hardenable monomer, photopatterning the dried paste and firing the patterned paste.

[0083] The substrate can be any material to which the paste composition will adhere. If the paste is non-conducting and a non-conducting substrate is used, a film of an electrical conductor to serve as the cathode electrode and provide means to apply a voltage to the electron emitting material will be needed. Silicon, a glass, a metal or a refractory material such as alumina can serve as the substrate. For display applications, the preferable substrate is glass and soda lime glass is

especially preferred. For optimum conductivity on glass, silver paste can be pre-fired onto the glass at 500-550° C. in air or in an inert gas such as nitrogen, but preferably in air, or the substrate may be coated with a layer of ITO. The conducting layer so-formed can then be over-printed with the emitter paste.

[0084] The paste used for conventional screen printing typically contains the electron emitting material, an organic medium, solvent, surfactant and either low softening point glass frit, metallic powder or metallic paint or a mixture thereof. The role of the medium and solvent is to suspend and disperse the particulate constituents, i.e. the solids, in the paste with a proper rheology for typical patterning processes such as screen printing. There are many organic media known for use for such purpose including cellulosic resins such as ethyl cellulose and alkyd resins of various molecular weights. Butyl carbitol, butyl carbitol acetate, dibutyl carbitol, dibutyl phthalate and terpineol are examples of useful solvents. These and other solvents are formulated to obtain the desired viscosity and volatility requirements.

[0085] A glass frit that softens sufficiently at the firing temperature to adhere to the substrate and to the electron emitting material is also used. A lead or bismuth glass frit can be used as well as other glasses with low softening points such as calcium or zinc borosilicates. If a screen printable composition with higher electrical conductivity is desired, the paste may also contain a metal, for example, silver or gold. The paste typically contains about 40 wt % to about 80 wt % solids based on the total weight of the paste. These solids include the electron emitting material and glass frit and/or metallic components. Variations in the composition can be used to adjust the viscosity and the final thickness of the printed material.

[0086] If the screen-printed paste is to be photopatterned, the paste may also contain a photoinitiator, a developable binder and a photohardenable monomer comprised, for example, of at least one addition polymerizable ethylenically unsaturated compound having at least one polymerizable ethylenic group. Typically, a paste prepared from an electron emitting material such as CNTs, silver and glass frit will contain about 0.01-6.0 wt % nanotubes, about 40-75 wt % silver in the form of fine silver particles and about 3-15 wt % glass frit based on the total weight of the paste.

[0087] The emitter paste is typically prepared by three-roll milling a mixture of the electron emitting material, organic medium, surfactant, solvent and either low softening point glass frit, metallic powder or metallic paint or a mixture thereof. The paste mixture can be screen printed using, for example, a 165-400-mesh stainless steel screen. The paste can be deposited as a continuous film or in the form of a desired pattern.

[0088] After printing, the conventionally-prepared electron field emitter is further processed by removing any residual photoresist material, drying the plate, and then installing it as the anode plate in an electrochemical cell. The cell is similar in construction to the cell described above, and the cathode therein may be stainless steel or any non-oxidizable conductor. The electrolyte, which is disposed between the cathode and the anode, contains boric acid and/or a borate compound. This embodiment of the methods hereof is generally performed by operation of the cell at a potential of less than about 10 volts, or in the range of from about 2 to about 6 volts, or in the range of from about 3 volts to about 5 volts. The cell may be operated for a period of time in the range of from about 1

to about 10 minutes, or in the range of from about 2 to about 6 minutes, or in the range of from about 3 to about 5 minutes.

[0089] After completion of operation of the cell, the plate may be removed from the cell, rinsed, dried and installed in such condition in a field emission device for use as part of the cathode assembly therein to provide electron emission in devices such as described above. Alternatively, however, before installation in a field emission device, the plate may first be baked and/or fired to melt the deposited polymer(s) and utilize them in that form as an adhesive to more securely anchor the CNTs to the surface of the plate, resulting in a CNT-containing film with excellent abrasion resistance. Firing may be performed at a temperature in the range of about 250° C. to about 650° C., or about 350° C. to about 550° C., or about 450° C. to about 525° C., for a period of time in the range of about 5 to about 30 minutes, or about 10 to about 25 minutes, or about 10 to about 20 minutes, in nitrogen or air. Higher firing temperatures can be used with substrates that can endure them provided the atmosphere is free of oxygen. However, the organic constituents in the paste are effectively volatilized at 350-450° C., leaving a layer of the composite of the electron emitting material and glass and/or metallic conductor.

[0090] In this embodiment of the methods hereof, where (as above) boric acid and/or a borate compound is present in the electrolyte solution, the material as deposited on the cell anode plate may thus include, in addition to the CNT complexes, some of the boric acid and/or borate compound. In such event, a further embodiment of this invention includes a film that is composed of a substrate and, disposed or deposited on the substrate, boric acid and/or a borate compound and a complex formed from carbon nanotubes and one or more anionic polymer(s).

[0091] In this embodiment, boric acid and/or a borate compound may be used in the electrolyte solution at a concentration therein in the range of about 0.1 wt % or more, or about 0.5 wt % or more, and yet about 10 wt % or less, or about 5 wt % or less.

[0092] Materials as used in the process hereof may be made by processes known in the art, or are available commercially from suppliers such as Alfa Aesar (Ward Hill, Mass.), City Chemical (West Haven, Conn.), Fisher Scientific (Fairlawn, N.J.), Sigma-Aldrich (St. Louis, Mo.) or Stanford Materials (Aliso Viejo, Calif.).

[0093] The advantageous attributes and effects of this invention may be seen in a series of examples (Examples 1-5), as described below. The embodiments on which the examples are based are representative only, and the selection of those embodiments to illustrate the invention does not indicate that materials, conditions, specifications, components, reactants, techniques and protocols not described in these examples are not suitable for practicing this invention, or that subject matter not described in these examples is excluded from the scope of the appended claims and equivalents thereof.

Examples

[0094] 150 mg of laser-ablated CNTs (from CNI, Houston, Tex.) was mixed with 30 mg yeast RNA (from Sigma Aldrich) in 15 mL of 1× TBE [tris borate (ethylenediaminetetraacetic acid)] buffer (from Sigma Aldrich). The mixture was sonicated with a probe sonicator at a power level of 20 W for 30 min. The resulting dispersion ("CNT Dispersion") was mixed with two other components according to the following table

(Table 1) to make up 100 mL of deposition solution. Ru²⁺(bipy)₃ as used in the deposition solution is tris(2,2'-bipyridyl)dichloro-ruthenium (II) and is obtained from Sigma Aldrich. EMMA is ethylene/methacrylic acid ionomer obtained from DuPont as Surlyn™ ionomer.

TABLE 1

Composition of Deposition Solution			
Component	Stock concentration	Volume added	Final conc.
CNT Dispersion	10 mg/mL	4 mL	0.04%
EMMA	10 mg/mL	2 mL	0.02%
Ru ²⁺ (bipy) ₃	10 mM	2 mL	0.2 mM
water		92 mL	

Example 1

[0095] A photoresist (PR) patterned glass substrate coated with indium tin oxide (ITO) (2"×2") (used as the cell anode) was prepared. The PR layer defines an array of open circular wells with 20 μm diameter. The open circular wells expose the ITO surface for CNT deposition. Before electrodeposition, the PR coated ITO plate was dipped into a solution of 0.01% Triton X-100 for 30 seconds, taken out and dried by blowing N₂ gas. This step is to coat the hydrophobic PR layer with a thin hydrophilic layer for better wetting.

[0096] After this treatment, a 2"×2" stainless steel plate (used as the cell cathode) and the PR-coated ITO plate (used as the cell anode) were inserted in a parallel fashion into a rectangular cell containing 15 mL of the deposition solution. FIG. 2 shows the rectangular cell containing deposition solution into which the stainless steel cathode and PR-coated anode are inserted in a parallel fashion. The electrochemical cell is designated as number 1, the slot for the cathode is designated as number 2 and the slot for the anode is designated as number 3.

[0097] A DC potential of 2.5 V (obtained from a Princeton Applied Research, Model 263A, Oak Ridge, Tenn.) was applied between the two electrodes. After 2 min, the deposition was stopped, and the ITO plate was taken out of the cell, rinsed with DI water and dried in air. The PR layer was stripped off by organic solvents such as acetone or a NMP:H₂O solution. The cell anode was then rinsed in DI H₂O and dried under flowing N₂ gas.

[0098] Control samples were made using the same laser ablated carbon nanotube powder from which the dispersion described above was derived. The nanotube powder was incorporated into a paste and screen printed onto a 2"×2" PR patterned ITO substrate. After imaging under UV exposure, the printed substrate was rinsed for 65 seconds in a NMP:H₂O solution.

[0099] Both the control and the electrochemically deposited substrates were fired in air in a 10-zone belt furnace (Lindberg, 810 thick-film conveyor, Watertown, Wis.) to 400° C. peak for 21 minutes. The substrates were then activated by placing an adhesive in contact with the patterned surface. Each activated substrate was then incorporated into a diode device as the cathode, with a 620 μm spacer between the 2"×2" ITO coated phosphor glass substrate that served as the anode. The diode thus formed was placed in a vacuum chamber evacuated to a base pressure below 1×10⁻⁵ Torr.

Example 2

[0100] A negative voltage pulse with a pulse width of 60 us at 60 Hz was applied to each diode using an IRCO high voltage source (Model F5k-10-02N, IRCO, Columbia Md.). The pulsing was supplied from a pulse generator (Stanford Research Systems, Inc., model DG535, Sunnyvale, Calif.). The resulting emission current was measured as a function of applied voltage using a Keithley 2000 multimeter (Keithley Instruments, Cleveland, Ohio). The field required to obtain 20 μA or more was noted. For the control sample, this field was found to be generally 4.5V/μm or greater. For the electrochemically deposited sample, the field was generally on the order of 2.5V/μm. FIG. 3 shows the average emission fields from the samples that were made from an electrochemical deposition (ECD) technique (square) and from a screen-printing (non ECD) technique (circle). Lower operational fields are preferred.

[0101] Carbon nanotube powder made from a laser ablation process was incorporated into a thick film paste and screen printed onto a 2"×2" photoresist (PR) patterned glass substrate coated with indium tin oxide (ITO). The PR layer defines an array of open circular wells with 20 μm diameter. The open wells expose the ITO surface onto which the CNT-containing paste can be screen printed. After imaging the printed surface under UV exposure, the substrate was rinsed for 65 seconds in a NMP:H₂O solution to reveal the patterned structure.

[0102] A 2"×2" stainless steel plate (used as the cell cathode) and the 2"×2" screen printed substrate on ITO (used as the cell anode) were inserted in a parallel fashion into a rectangular cell (as shown in FIG. 2) containing 15 mL of electrolyte solution (1× TBE or 0.1 M Boric acid, Sigma Aldrich). A DC potential of 3V (Princeton Applied Research, Model 263A) was applied between the two electrodes. After 4 min, the treatment was stopped, and the ITO plate was taken out of the cell, and allowed to dry in air.

[0103] The substrate (cell anode) was then fired in air to 400° C. peak for 21 minutes in a 10-zone belt furnace (Lindberg, 810 thick-film conveyor, Watertown, Wis.). The substrate was then activated by placing an adhesive in contact with the patterned surface containing the carbon nanotube paste. The substrate was then incorporated into a diode device as the cathode, separated from the ITO coated phosphor glass anode by a 620 μm spacer. The diode thus formed was placed in a vacuum chamber evacuated to a base pressure below 1×10⁻⁵ Torr.

[0104] A negative voltage pulse with a pulse width of 60 us at 60 Hz was applied using an IRCO high voltage source (Model F5k-10-02N, IRCO, Columbia, Md.). The pulsing was supplied from a pulse generator (Stanford Research Systems, Inc., Model DG535, Sunnyvale, Calif.). The resulting emission current was measured as a function of applied voltage using a Keithley 2000 multimeter (Keithley Instruments, Cleveland, Ohio). The field required to obtain 20 μA or more was noted.

[0105] For a control sample not subjected to electrochemical treatment, this field was found to be generally greater than 5V/μm. For the electrochemically treated sample, the fields needed were generally on the order of 2.5V/μm to 3.0V/μm. FIG. 4 shows the emission curves from screen printed samples that were either treated in an electrochemical cell

(solid lines) or not treated in an electrochemical cell (dotted lines). Lower operational fields for any given current are preferred.

[0106] Features of certain of the devices of this invention are described herein in the context of one or more specific embodiments that combine various such features together. The scope of the invention is not, however, limited by the description of only certain features within any specific embodiment, and the invention also includes (1) a subcombination of fewer than all of the features of any described embodiment, which subcombination may be characterized by the absence of the features omitted to form the subcombination; (2) each of the features, individually, included within the combination of any described embodiment; and (3) other combinations of features formed by grouping only selected features of two or more described embodiments, optionally together with other features as disclosed elsewhere herein.

[0107] In this specification, unless explicitly stated otherwise or indicated to the contrary by the context of usage, where an embodiment of the subject matter hereof is stated or described as comprising, including, containing, having, being composed of or being constituted by or of certain features or elements, one or more features or elements in addition to those explicitly stated or described may be present in the embodiment. An alternative embodiment of the subject matter hereof, however, may be stated or described as consisting essentially of certain features or elements, in which embodiment features or elements that would materially alter the principle of operation or the distinguishing characteristics of the embodiment are not present therein. A further alternative embodiment of the subject matter hereof may be stated or described as consisting of certain features or elements, in which embodiment, or in insubstantial variations thereof, only the features or elements specifically stated or described are present.

1. A method for the deposition of carbon nanotubes, comprising:

- (a) providing an electrochemical cell that comprises a cathode, an anode plate, a first electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate;
- (b) providing as an aqueous electrolyte disposed between the cathode and the anode a dispersion of a complex formed from carbon nanotubes and a first anionic polymer;
- (c) applying a voltage to the electrochemical cell to deposit the complex on the anode; and
- (d) removing the anode plate from the electrochemical cell and firing the plate in air.

2. A method according to claim 1 wherein the aqueous electrolyte further comprises a coagulant.

3. A method according to claim 2 wherein coagulant residue is deposited on the anode together with the complex.

4. A method according to claim 1 wherein the first polymer comprises a nucleic acid molecule.

5. A method according to claim 1 wherein the first polymer comprises RNA.

6. A method according to claim 1 wherein the electrolyte further comprises a second anionic polymer.

7. A method according to claim 6 wherein the second ionic polymer comprises a styrenic ionomer or an ionized ethylene/(meth)acrylic acid

8. A method according to claim 6 wherein the complex, as deposited on the anode, is deposited in a matrix of the second anionic polymer.

9. A method according to claim 7 wherein the first polymer comprises a nucleic acid molecule.

10. A method according to claim 1 further comprising a step of removing the anode plate from the cell, and installing it in a field emission device.

11. A method for the deposition of carbon nanotubes, comprising:

- (a) providing an electrochemical cell that comprises a cathode, an anode plate, a first electrically conducting pathway connecting the cathode to an electrical power supply, and a second electrically conducting pathway connecting the electrical power supply to the anode plate;
- (b) providing an aqueous electrolyte disposed between the cathode and the anode, wherein the electrolyte comprises boric acid and/or a borate compound, and a dispersion of a complex formed from carbon nanotubes and a first anionic polymer; and
- (c) applying a voltage to the electrochemical cell to deposit the complex on the anode.

12. A method according to claim 11 wherein boric acid and/or a borate compound is deposited on the anode together with the complex.

13. A method according to claim 11 wherein the aqueous electrolyte further comprises a coagulant.

14. A method according to claim 13 wherein coagulant residue is deposited on the anode together with the complex.

15. A method according to claim 11 wherein the first polymer comprises a nucleic acid molecule.

16. A method according to claim 11 wherein the first polymer comprises RNA.

17. A method according to claim 11 wherein the electrolyte further comprises a second anionic polymer.

18. A method according to claim 17 wherein the second ionic polymer comprises a styrenic ionomer or an ionized ethylene/(meth)acrylic acid copolymer.

19. A method according to claim 17 wherein the first polymer comprises a nucleic acid molecule.

20. A method according to claim 11 further comprising a step of removing the anode plate from the cell, and installing it in a field emission device.

21. A film comprising a substrate and, disposed on the substrate, (a) boric acid and/or a borate compound, and (b) a complex formed from carbon nanotubes and a first anionic polymer.

22-28. (canceled)

29. A cathode assembly for a field emission device comprising a film according to claim 21.

30. A field emission device comprising a cathode assembly according to claim 29.

31-35. (canceled)

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