COATED METAL OXIDE NANOPARTICLES AND METHODS FOR PRODUCING SAME

ACKNOWLEDGEMENT

[0001] This invention was made with government support under Grant Nos. N00014-03-1-0731 and N0014-05-1-0760 awarded by the Office of Naval Research. The government has certain rights in the invention.

CROSS-REFERNCE TO RELATED APPLICATIONS

[0002] This application claims the priority of United States Provisional Application No. 60/680,382, filed May 12, 2005, which is hereby incorporated herein by reference in its entirety.

BACKGROUND

[0003] As the trend towards the miniaturization of electronic circuits continues, decreasing the size of integrated devices becomes desirable. Capacitors are one such fundamentally important device, and, with increasing circuit-size reduction, their effective area is concomitantly decreased, making it problematical to achieve a desired capacitance using a conventional dielectric film between the elements of the capacitors. Future high-performance multilayered ceramic capacitors are estimated to require dielectric films with thicknesses less than 0.5 μm. Certain ceramic/polymer composites have been investigated for use in thin-film integral capacitors; in attempts to combine the high dielectric constants of ceramics with the high dielectric breakdown strength, processibility, and low cost of polymers. However, in known nanocomposite materials, success in achieving the desired composite properties by mixing high-dielectric ceramic powders with polymers has been limited by the high viscosity of ceramic/polymer mixtures and by ceramic particle coagulation and/or low solubility of the ceramic materials, typically resulting in unacceptable film quality, leading to dielectric composites with low electric-field breakdown strength, high dielectric loss and poor mechanical strength.

[0004] Therefore, despite conventional materials known to those of ordinary skill in the art, there remains a need for ceramic materials having an improved compatibility with

polymeric materials, or nanoparticles comprising coatings having other desirable properties, so as to allow the preparation of nanocomposite films having properties tailored for use in a variety of electronic and microelectronic applications, so as to overcome the deficiencies of the prior art.

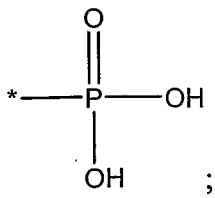
SUMMARY

[0005] The various inventions disclosed and described herein relate to methods for modifying or improving the properties of ceramic nanoparticles, such as for example their compatibility with polymers, so as form new ceramic/polymer nanocomposite materials with new and improved properties, and uses of those improved materials in electronic and microelectronics applications.

[0006] In some aspects, disclosed are coated metal oxide nanoparticles comprising a metal oxide nanoparticle having a surface; and phosphonic acid ligands attached to the metal oxide nanoparticle surface.

[0007] Also disclosed are coated metal oxide nanoparticles comprising a metal oxide nanoparticle having a surface; and ligands selected from residues of phosphonic acids, thiophosphonic acids, dithiophosphonic acids, trithiophosphonic acids, phosphinic acids, thiophosphinic acids, dithiophosphinic acids, phosphohydroxamic acids, and thiophosphohydroxamic acids and derivatives thereof and mixtures thereof attached to the metal oxide nanoparticle surface.

[0008] Also disclosed are phosphonic acid compounds comprising the structure Gn-R-Xn, wherein G is a terminal group; wherein R is a bridging group; wherein X is a phosphonic acid group having the structure:



; and

wherein each n is, independently, 1, 2, or 3. Such phosphonic acid compounds can be useful for the preparation of coated metal oxide nanoparticles and/or nanocomposites.

[0009] In related aspects, also disclosed are methods for preparing coated metal oxide nanoparticles comprising the steps of providing the metal oxide nanoparticles; and reacting the metal oxide nanoparticles with the phosphonic acid or an ester or salt thereof, so as to attach at least some of the phosphonic acid to the metal oxide nanoparticle surface, to form a coated metal oxide nanoparticle.

[0010] Also disclosed are methods for preparing coated metal oxide nanoparticles comprising the steps of treating a metal oxide nanoparticle with an etchant; and reacting the etched metal oxide nanoparticle with a phosphonic acid compound having an anchoring group that can bind to the metal oxide nanoparticle.

[0011] In some aspects, the inventions disclosed herein relate to methods for preparing coated nanoparticles comprising the steps of treating a metal oxide nanoparticle with an etchant; and reacting the etched metal oxide nanoparticle with a phosphonic acid compound having an anchoring group that can bind to the metal oxide nanoparticle.

[0012] In additional related aspects, disclosed herein are methods for preparing a film comprising the steps of dispersing a coated metal oxide nanoparticle in a solvent; dissolving a polymer in the solvent to form a solution or dispersion of the polymer and coated metal oxide nanoparticles; and forming a film comprising a nanocomposite.

[0013] Also disclosed are the products of the disclosed methods.

[0014] Also disclosed are nanocomposite compositions comprising a polymer and a coated metal oxide nanoparticle dispersed within the polymer.

[0015] Also disclosed are articles, films, and capacitors comprising a coated metal oxide nanoparticle or a nanocomposite.

[0016] Also disclosed are the products of the methods of the invention.

[0017] Additional aspects of the inventions described and disclosed herein, and advantages of the inventions disclosed herein are set forth in part in the description which follows, and in part can be obvious from the description, or can be learned by practice. Other advantages can be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general

disclosures and the following detailed description are exemplary and explanatory only and are not to be interpreted as restrictive of the inventions actually claimed.

BRIEF DESCRIPTION OF THE FIGURES

[0018] The accompanying Figures, which are incorporated in and constitute a part of this specification, illustrate several embodiments and together with the description serve to explain the principles of the invention.

[0019] Figure 1 shows some target phosphonic acids for metal-oxide-nanoparticle functionalization. Here n represents an alkyl chain, *e.g.* C_2-C_{16}.

[0020] Figure 2 shows phosphonic acids with functional groups suitable for cross-linking to polymers. Here n represents an alkyl chain, *e.g.* C_2-C_{16}.

[0021] Figure 3 shows (a) Phosphonic acids with polymerizable groups. Here n represents an alkyl chain *e.g.* C_2-C_{16}. (b) Synthesis of an iodide-terminated polymer by ROMP and subsequent conversion to a phosphonic-acid terminated polymer.

[0022] Figure 4 shows TGA of *n*-octyphosphonic acid modified particles and unmodified $BaTiO_3$.

[0023] Figure 5 shows selected FT-IR spectra of coated $BaTiO_3$ nanoparticles (70nm, Aldrich). The x-axes units are in wavenumbers (cm^{-1}). Each spectrum shows surface modified $BaTiO_3$ with (a) OPA, (b) MPA, (c) HUPA, (d) ODPA, (e) DPPA, (f) FOPA, (g) TPDPA. (h) TKYNPA, and (i) is spectrum of unmodified $BaCO_3$ free-$BaTiO_3$.

[0024] Figure 6 shows selected FT-IR spectra of $BaTiO_3$ nanoparticles coated with mixtures of phosphonic acid. The x-axes units are in wavenumbers (cm^{-1}). (a) OPA+FOPA obtained by treating the surface with 1:1 (molar ratio) mixture of ligands, (b) OPA+TPDPA obtained by exchanging OPA ligand with TPDPA ligand.

[0025] Figure 7 shows IR spectra of nanocrystalline metal oxide powders after modification with *n*-octyphosphonic acid.

[0026] Figure 8 shows (a) powder XRD patterns of commercial nanocrystalline metal oxide powders before (solid line) and after (dotted line) modification with *n*-octylphosphonic acid.

SEM images of (b) $BaTiO_3$; (c) $BaZr_{0.2}Ti_{0.8}O_3$; (d) $SrTiO_3$ after modification.

[0027] Figure 9 shows absorption spectra of TPD phosphonic acid (TPDPA), $BaTiO_3$ nanoparticles (BT) and $BaTiO_3$ nanoparticles coated with TPD phosphonic acid (TPDBT) in MeCN.

[0028] Figure 10 shows emission (top) and excitation (bottom) spectra of $BaTiO_3$ nanoparticles coated with TPD phosphonic acid (TPDBT) in MeCN.

[0029] Figure 11 shows generalized synthesis of phosphonic acids *via* Arbuzov reaction/hydrolysis.

[0030] Figure 12 shows schematics of transetherification by HMMM on a polymer chain with hydroxyl side groups.

[0031] Figure 13 shows TGA of unmodified BT and surface-modified BTs. Only the phosphonic acid coated particles showed significant weight loss at high temperature.

[0032] Figure 14 shows TGA of n-OPA coated on "as received" BT.

[0033] Figure 15 shows TGA of various phosphonic acid ligands coated on BT. The weight loss increased with increasing the molecular weight of phosphonic acids used.

[0034] Figure 16 shows TGA comparison of P(VBPA) and P(VBPA)-BT.

[0035] Figure 17 shows characterization results from BT:PVP thin films on ITO/glass.

[0036] Figure 18 shows SEM images of 75% vol. PFBZPA-BT:Viton film. Top surface (left column) and cross-section prepared by low temperature fracture (right column). There were many cracks on the top surface observed at low magnification and many voids (air packets) observed at high magnification. The cross-sectional image showed large pinhole across the film and delamination but did not show sedimentation.

[0037] Figure 19 shows FT-IR spectra from kinetics study.

[0038] Figure 20 shows average dielectric constants measured from different polymer-barium titanate nanocomposites. All the composites contained 50 % nanoparticles by

volume. BP-B: unmodified $BaTiO_3$/polycarbonate with BYK-w-9010, PBP: PEGPA-modified $BaTiO_3$/polycarbonate, PBP-B: PEGPA-modified $BaTiO_3$/polycarbonate with BYK-w-9010, FBP: PFBZPA-modified $BaTiO_3$/polycarbonate, BV-B: unmodified $BaTiO_3$/Viton with BYK-w-9010, FBV: PFBZPA-modified $BaTiO_3$/Viton, FBV-B: PFBZPA-modified $BaTiO_3$/Viton with BYK-w-9010.

[0039] Figure 21 shows leakage current measured by applying up to 100 V_{DC} across thin film capacitors. Top: polycarbonate-based devices. Bottom: P(VDF-HFP)-based devices. Raw data was filtered using a low pass filter to remove bad data points and fit by an exponential growth function.

[0040] Figure 22 shows capacitance and loss tangent measured as a function of frequency for representative devices based on $BaTiO_3$/polycarbonate and $BaTiO_3$/P(VDF-HFP).

[0041] Figure 23 shows dielectric breakdown field measured for different devices.

[0042] Figure 24 shows maximum energy stored at 1 MHz in a hypothetical 1 cm^2 area and 1 μm thick capacitor device made with the different compositions studied.

[0043] Figure 25 shows powder XRD of new BT (TPL), old BT (Aldrich), and sintered tetragonal BT (synthesized by SCJ). The splitting of (002) and (200) peaks around 45 degree is associated with the relative tetragonality (a/c ratio, a and c are two different lattice parameters), i.e. the higher the splitting, the higher the a/c ratio or tetragonality.

[0044] Figure 26 shows a SEM micrograph of BT150 showing its average size and shape.

[0045] Figure 27 shows SEM micrographs of the 50:50 vol. BT:polycarbonate nanocomposite films. Top: unmodified BT with BYK-w-9010, Middle: PEGPA-BT without BYK-w-9010, and Bottom: PEGPA-BT with BYK-w-9010.

[0046] Figure 28 shows SEM micrographs of the 50:50 vol. BT-Viton nanocomposite films. Top: unmodified BT with BYK-w-9010, Middle: PFBZPA-BT without BYK-w-9010, and Bottom: PFBZPA-BT with BYK-w-9010.

[0047] Figure 29 shows FT-IR spectra of BT150. As received (upper), and after washing with NH_4Cl (lower).

[0048] Figure 30 shows normalized FT-IR absorbance spectra of dried BT nanoparticles from different manufacturers showing different amount of surface hydroxyl groups and barium carbonate. Aldrich: 30-50 nm, TPL: 150 nm, Inframat: 100 nm, BT8: 120-160 nm, BT16: ~50 nm.

[0049] Figure 31 shows: Top: PFBZPA-modified BT150, Bottom: PFGPA-modified BT150.

[0050] Figure 32 shows dielectric constants measured from capacitor devices fabricated using BT150 nanoparticles. The volume fraction of BT150 is 50 %. The prefix P and F of "BT" stands for the phosphonic acid ligands PEGPA and PFBZPA, respectively. The suffix P and V of "BT" stands for the host matrix PC and Viton, respectively. The suffix B stands for the use of 5 wt. % BYK-w-9010. Both 50PBTP and 50FBTV resulted in smaller dielectric constant implying poor film quality. The amount of BYK-w-9010 was not optimized and a little larger than other reported "best" amount (e.g. ~2 wt. % for BT8).

[0051] Figure 33 shows a contour plot showing the effective dielectric constant of a nanocomposite made of $BaTiO_3$ (k = 1000) in a host matrix with varying permittivity at various nanoparticle volume fractions.

[0052] Figure 34 shows FT-IR spectra of pure ACPA (upper) and ACPA-modified P25 (lower).

[0053] Figure 35 shows infrared absorption spectra of 70 nm diameter $BaTiO_3$ (Aldrich) treated with different anchoring groups with same length of alkyl ($-C_8H_{17}$) chain. (phosphonic acid: PH, sulfonate: SU, trimethoxysilane: SI, and carboxylic acid: CA). Note that the phosphonic acid-treated particles show the most intense C-H stretch (*ca.* 2900 cm^{-1}).

[0054] Figure 36 shows energy dispersive x-ray spectroscopy of uncoated (top) and n-octylphosphonic acid coated (bottom) 70 nm $BaTiO_3$ nanoparticles. The data in the bottom plot shows the presence of phosphorus and increase in carbon and oxygen due to the ligand coating.

[0055] Figure 37 shows XPS survey scan spectra of both uncoated and *n*-octyphosphonic acid-coated BT. Note that the presence of phosphorous peak and increase in C1s peak height

after modification (OPABT). The decrease in peak height of Ba3d and O1s is due to the loss of $BaCO_3$ upon treating with phosphonic acid.

[0056] Figure 38 shows exemplary phosphonic acid ligands from Table 2 used to modify surface of $BaTiO_3$ nanoparticles.

[0057] Figure 39 shows superposition of nanocomposite (top) and *n*-octadecylphosphonic acid (bottom) DP-MAS ^{31}P SSNMR spectra.

[0058] Figure 40 shows DP (upper) and CP (lower) MAS ^{31}P SSNMR spectra of *n*-octadecylphosphonic acid (top) and *n*-octadecylphosphonic acid-coated $BaTiO_3$.

[0059] Figure 41 shows IR spectra of $BaTiO_3$ nanopowder after treatment with *n*-octyl organic ligands.

DETAILED DESCRIPTION

[0060] Before the present compounds, compositions, articles, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

A. DEFINITIONS

[0061] Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0062] Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of

publication provided herein can be different from the actual publication dates, which may need to be independently confirmed.

[0063] As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a compound," "a substrate," or "a metal" includes mixtures of two or more such compounds, substrates, or metals, and the like.

[0064] Ranges can be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it can be understood that the particular value forms another embodiment. It can be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as "about" that particular value in addition to the value itself. For example, if the value "10" is disclosed, then "about 10" is also disclosed. It is also understood that when a value is disclosed that "less than or equal to" the value, "greater than or equal to the value" and possible ranges between values are also disclosed, as appropriately understood by the skilled artisan. For example, if the value "10" is disclosed the "less than or equal to 10" as well as "greater than or equal to 10" is also disclosed. It is also understood that throughout the application, data is provided in a number of different formats and that this data represents endpoints and starting points, and ranges for any combination of the data points. For example, if a particular data point "10" and a particular data point 15 are disclosed, it is understood that greater than, greater than or equal to, less than, less than or equal to, and equal to 10 and 15 are considered disclosed as well as between 10 and 15. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0065] A residue of a chemical species, as used in the specification and concluding claims, refers to the moiety that is the resulting product of the chemical species in a particular reaction scheme or subsequent formulation or chemical product, regardless of whether the moiety is actually obtained from the chemical species. Thus, an ethylene glycol residue in a

polyester refers to one or more -OCH_2CH_2O- units in the polyester, regardless of whether ethylene glycol was used to prepare the polyester. Similarly, a sebacic acid residue in a polyester refers to one or more -$CO(CH_2)_8CO$- moieties in the polyester, regardless of whether the residue is obtained by reacting sebacic acid or an ester thereof to obtain the polyester.

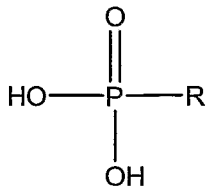
[0066] As used herein, the terms "optional" or "optionally" means that the subsequently described event or circumstance can or can not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0067] As used herein, unless expressly defined otherwise, the term "alkyl" can refer to a hydrocarbon group that can be conceptually formed from an alkane, alkene, or alkyne by removing hydrogen from the structure of a cyclic or non-cyclic hydrocarbon compound having straight or branched carbon chains, and replacing the hydrogen atom with another atom or organic or inorganic substituent group. In some aspects of the invention, the alkyl groups are "C_1 to C_6 alkyl" such as methyl, ethyl, propyl, isopropyl, *n*-butyl, *iso*-butyl, *sec*-butyl, *tert*-butyl, amyl, *tert*-amyl, and hexyl groups, their alkenyl analogues, their alkynyl analogues, and the like. Many embodiments of the invention comprise "C_1 to C_4 alkyl" groups (alternatively termed "lower alkyl" groups) that include methyl, ethyl, propyl, iso-propyl n-butyl, iso-butyl, sec-butyl, and t-butyl groups, their alkenyl analogues, their alkynyl analogues, or the like. Some of the preferred alkyl groups of the invention have three or more carbon atoms preferably 3 to 16 carbon atoms, 4 to 14 carbon atoms, or 6 to 12 carbon atoms. The alkyl group can be unsubstituted or substituted. A hydrocarbon residue, for example an alkyl group, when described as "substituted," contains or is substituted with one or more independently selected heteroatoms such as O, S, N, P, or the halogens (fluorine, chlorine, bromine, and iodine), or one or more substituent groups containing heteroatoms (OH, NH_2, NO_2, SO_3H, and the like) over and above the carbon and hydrogen atoms of the substituent residue. Substituted hydrocarbon residues can also contain carbonyl groups, amino groups, hydroxyl groups and the like, or contain heteroatoms inserted into the "backbone" of the hydrocarbon residue. In one aspect, an "alkyl" group can be fluorine substituted. In a further aspect, an "alkyl" group can be perfluorinated.

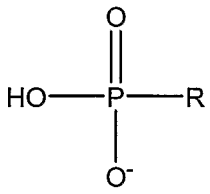
[0068] As used herein, the term "nanoparticle" refers to a particle comprising a solid core of

a material (for example, an inorganic metal oxide material comprising an at least partially ordered three dimensional array of metal cations and oxide anions), the particle having varying shapes and longest linear dimension of from about 1 nm to about 1000 nanometers.

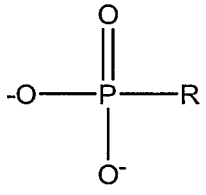
[0069] As used herein, the term "phosphonic acid" refers an organic compound having the structure:



wherein R is an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. Those of ordinary skill in the art are aware that the hydrogens attached to the OH groups of phosphonic acids are acidic and can be removed by bases or at appropriate pH's to form salts of the phosphonic acids having phosphonate mono or di-anions having the structure:



phosphonate anion

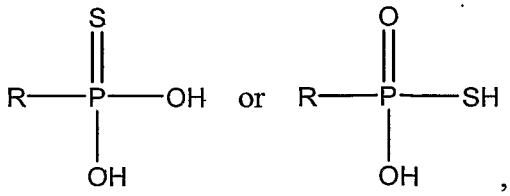


phosphonate dianion

[0070] It is understood that, when present as an anion, the phosphonate can include one or more associated counter ions, for example, monovalent cations including lithium, sodium, or potassium or one or more divalent cations including calcium or zinc. The organic "R" radical or residue comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons,

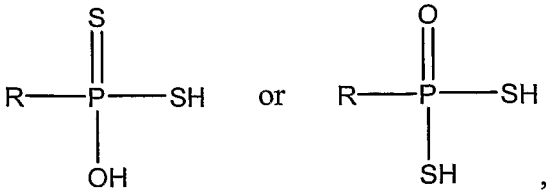
polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the phosphonates comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms.

[0071] As used herein, the term "thiophosphonic acid" refers an organic compound having the structure:



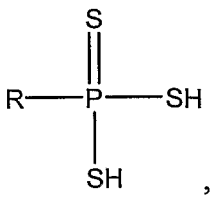
wherein R is an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. The organic "R" radical or residue comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

[0072] As used herein, the term "dithiophosphonic acid" refers an organic compound having the structure:



wherein R is an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. The organic "R" radical or residue comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

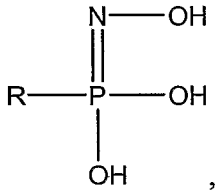
[0073] As used herein, the term "trithiophosphonic acid" refers an organic compound having the structure:



wherein R is an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. The organic "R" radical or residue comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The

R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

[0074] As used herein, the term "phosphohydroxamic acid" refers an organic compound having the structure:

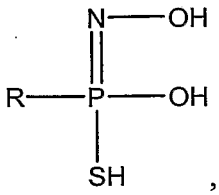


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wherein R is an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. The organic "R" radical or residue comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4

carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

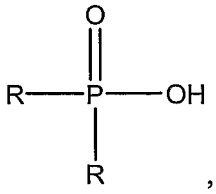
[0075] As used herein, the term "thiophosphohydroxamic acid" refers an organic compound having the structure:



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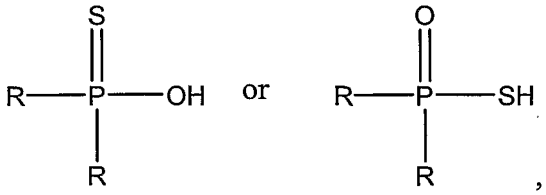
wherein R is an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. The organic "R" radical or residue comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

[0076] As used herein, the term "phosphinic acid" refers an organic compound having the structure:



wherein each R is, independently, an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. Each organic "R" radical or residue independently comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

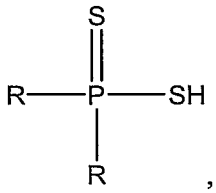
[0077] As used herein, the term "thiophosphinic acid" refers an organic compound having the structure:



wherein each R is, independently, an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. Each organic "R" radical or residue independently comprises at least one carbon atom, and includes but is not limited

to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

[0078] As used herein, the term "dithiophosphinic acid" refers an organic compound having the structure:

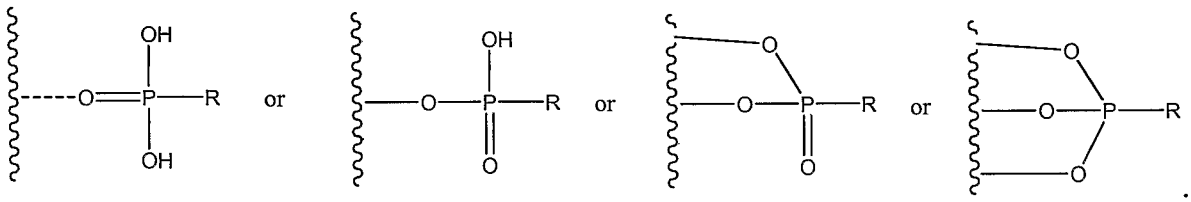


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wherein each R is, independently, an organic (carbon-containing) radical or residue wherein the phosphorus atom is bonded to a carbon atom of the R group. Each organic "R" radical or residue independently comprises at least one carbon atom, and includes but is not limited to the many well-known carbon-containing groups, residues, or radicals well known to those of ordinary skill in the art. The R radicals can contain various heteroatoms, or be bonded to another molecule through a heteroatom, including oxygen, nitrogen, sulfur, phosphorus, or the like. Examples of suitable R radicals include but are not limited to alkyls such as methyl, butyl, or octadecyl radicals and the like, or substituted alkyls such as hydroxymethyls, haloalkyls, aromatics such as phenyls or substituted aromatics, such as phenols or anilines; or polymeric residues such as polyethylene, fluoropolymers such as

Teflons or Vitons, polycarbonates, etc, and the like. In many non-polymeric embodiments, the R radicals of the compounds comprise 1 to 18 carbon atoms, 1 to 15, carbon atoms, 1 to 12 carbon atoms, 1 to 8 carbon atoms, or 1 to 4 carbon atoms. In a yet further aspect, the compounds can be substituted or functionalized with the bridging and/or terminal groups, as disclosed herein. Those of ordinary skill in the art are aware that corresponding anion(s) can be formed by treatment with bases or at appropriate pH's to form corresponding salts. It is also understood that, when present as anions, the compounds can include one or more associated counter ions.

[0079] As used herein, the term "ligand" includes structures wherein one or more acidic protons are absent from the compound and one or more oxygen or sulfur atoms are attached or bonded to the surface, as illustrated below:



[0080] As used herein, the term "polymer" refers to a relatively high molecular weight (when compared to the monomeric unit) macromolecule made up of multiple (*i.e*, three or more) repeating units. The repeating units, or monomers, can be the same or different. Those of skill in the art of polymer chemistry can readily recognize polymeric structures. The term polymer includes a copolymer: a polymer formed from two or more polymers. By way of example and without limitation, a copolymer can be an alternating copolymer, a random copolymer, a block copolymer, or a graft copolymer. In one aspect, a copolymer can be a segmented polymer.

[0081] Disclosed are the components to be used to prepare the compositions as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds can not be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications

that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the methods.

[0082] It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions, and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result.

B. COATED METAL OXIDE NANOPARTICLES

[0083] The present invention relates generally to surface coatings of metal oxide nanoparticles by organic ligands and mixtures of organic ligands and the uses of such particles and/or nanocomposites incorporating such particles. The present invention provides compositions of ligand coated metal oxide nanoparticles that offer control of surface energy, solubility, and dispersability in organic or polymeric matrices, and reduction of agglomeration in such media. The invention further provides for the attachment of a wide range of terminal groups that can impart specific chemical, optical, electronic, and/or sensing properties to the coated nanoparticles.

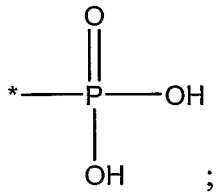
[0084] In one aspect, the coated nanoparticles of the present invention are useful when incorporated into solutions or suspensions, prepolymers, and polymers. The compositions can allow for tailoring of the rate of dissolution or achieving homogeneous suspension in a

variety of host media, including liquids and polymeric hosts, by changing the nature of the ligands or terminal groups attached to the ligand.

[0085] The term "metal oxide nanoparticle" as used herein refers to a particle comprising a solid core of an inorganic metal oxide material comprising an at least partially ordered three dimensional array of metallic cations and oxide anions, the particle having varying shapes and longest linear dimension of from about 1 nm to about 1000 nanometers. Those of ordinary skill in the arts related to the composition and structures of inorganic solids, minerals and ceramics are aware of a very large number of solid metal oxide minerals and/or ceramics, such as the large and well known class of perovskites. Some such metal oxide materials have a well defined chemical composition (e.g., stoichiometric metal oxides having a well defined composition, such as $BaTiO_3$), while some "non-stoichiometric" metallic oxides have variable proportions of mixtures of the metal cations, such as for example $BaTi_{0.8}Zr_{0.2}O_3$ or those with metal and/or oxygen ion vacancies. In certain aspects, such nanoparticles can comprise either irregularly shaped nanoparticles or "nanospheres."

[0086] In one aspect, the invention relates to a coated metal oxide nanoparticle comprising a metal oxide nanoparticle having a surface; and phosphonic acid ligands attached to the metal oxide nanoparticle surface.

[0087] In a further aspect, the invention relates to a coated metal oxide nanoparticle, wherein the at least one phosphonic acid ligand comprises a residue of a compound having the structure G_n-R-X_n, wherein G is a terminal group; wherein R is a bridging group; wherein X is a phosphonic acid group having the structure:



; and

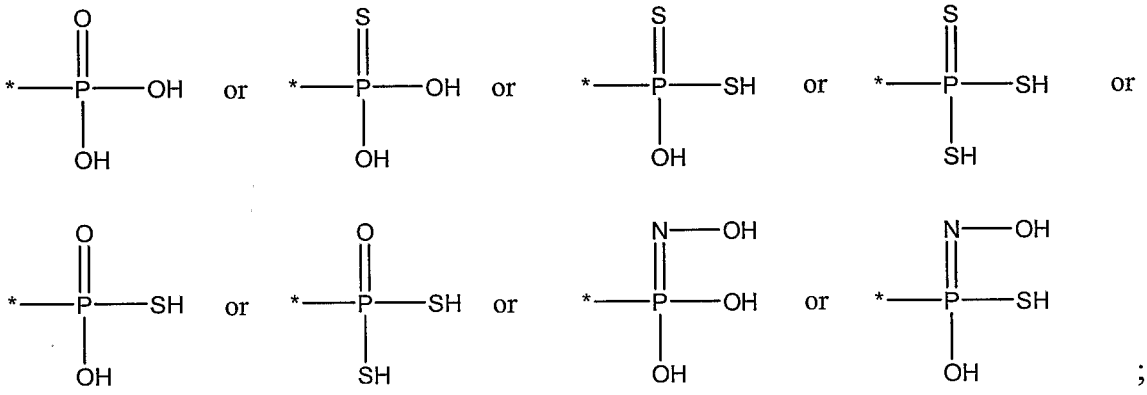
wherein each n is, independently, 1, 2, or 3.

[0088] In a yet further aspect, each n is 1. In a still further aspect, the compound comprises the structure G-R-X.

[0089] In a further aspect, the invention relates to a coated metal oxide nanoparticle

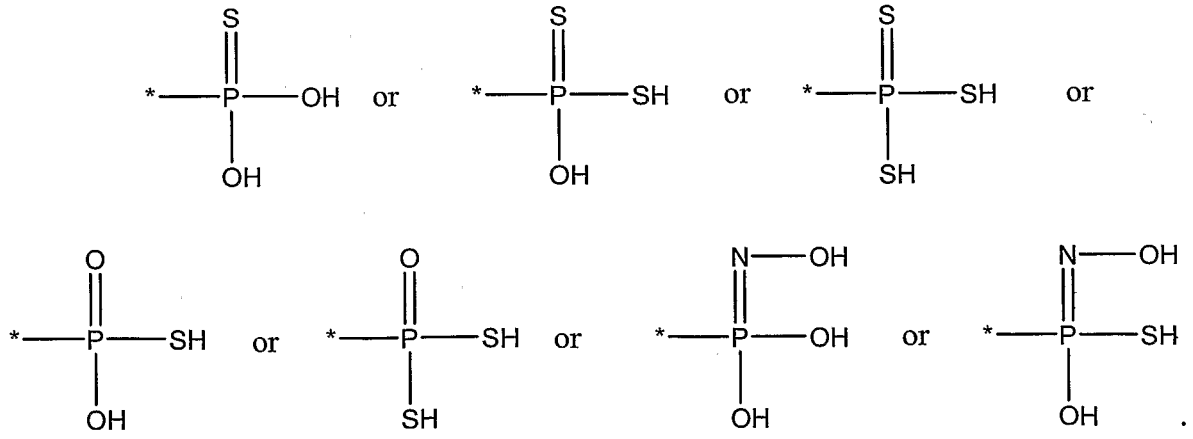
comprising a metal oxide nanoparticle having a surface; and ligands selected from residues of phosphonic acids, thiophosphonic acids, dithiophosphonic acids, trithiophosphonic acids, phosphinic acids, thiophosphinic acids, dithiophosphinic acids, phosphohydroxamic acids, and thiophosphohydroxamic acids and derivatives thereof and mixtures thereof attached to the metal oxide nanoparticle surface.

[0090] In a further aspect, the ligands comprise residues of compounds having the structure: G_n-R-X_n, wherein G is a terminal group; wherein R is a bridging group; wherein X is selected from:

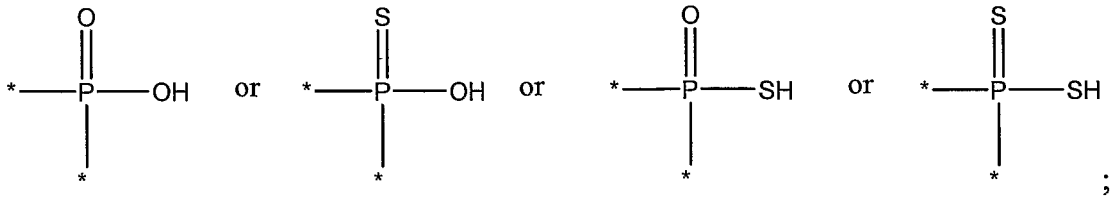


and wherein each n is, independently, 1, 2, or 3.

[0091] In a further aspect, X is selected from:



[0092] In a yet further aspect, the ligands comprise residues of compounds having the structure: G_n-R-X_n, wherein G is a terminal group; wherein R is a bridging group; wherein X is selected from:



and wherein each n is, independently, 1, 2, or 3. In certain aspects, each n is 1. In certain further aspects, the compound comprises the structure G-R-X.

1. PARTICLE COMPOSITION

[0093] In one aspect, the coated metal oxide nanoparticle can comprise a coated metal oxide nanoparticle. For example, the nanoparticle can comprise a binary, quarternary, or higher order metal oxide or mixture thereof. Binary metal oxides comprise cations of one metallic element and oxygen anions, ternary metal oxides comprise cations of two metallic elements and oxide anions, quarternary metal oxides have cations derived from three metallic elements and oxygen anions, etc. In a further aspect, a metal oxide nanoparticle can comprise one or more perovskites, distorted perovskites, or a mixture thereof.

[0094] In a further aspect, a coated metal oxide nanoparticle can have the formula ABO_3, wherein A and B are metal cations of different sizes. In a further aspect, in a coated metal oxide nanoparticle of the invention, at least one of the perovskites has the ternary formula ABO_3, wherein A and B are metal cations of different sizes, where A is a metal cation selected from Ba, Sr, Pb and mixtures thereof and B is a metal cation selected from Ti, Zr, Hf, and mixtures thereof. In a further aspect, in a coated metal oxide nanoparticle of the invention, at least one of the perovskites has the formula $ATiO_3$, wherein A is a metal cation selected from Barium and Strontium.

[0095] In one aspect, the coated metal oxide nanoparticles and/or nanocomposites of the invention can be selected to exclude any particular disclosed metal oxide species. For example, in one aspect, the coated metal oxide nanoparticles and/or nanocomposites of the invention can be limited to ternary or higher order metal oxides. As a further example, in one aspect, the coated metal oxide nanoparticles and/or nanocomposites of the invention can be limited to metal oxides having a perovskite structure.

[0096] It is understood that any particular metal oxide can be excluded from coated metal

oxide nanoparticles and/or nanocomposites of the invention. For example, in one aspect, TiO_2 and/or Al_2O_3 can be substantially absent from the coated metal oxide nanoparticles and/or nanocomposites of the invention. In a further aspect, TiO_2 and/or Al_2O_3 nanoparticles can be absent from the coated metal oxide nanoparticles and/or nanocomposites of the invention.

[0097] In a further aspect, at least one of the perovskites is a distorted perovskite having the ternary formula $A_{(1-x)}B_{(1+x)}O_3$, wherein A and B are metal cations of different sizes and x is a number less than 1 and greater than zero 0. In a yet further aspect, A and B are selected from the group consisting of titanium, manganese, copper, tungsten, niobium, bismuth, zirconium, lead, lithium, strontium, lanthanum, and ruthenium. In related aspects, the metal oxide nanoparticle can comprise quarternary metal oxides such as $Pb(Zr,Ti)O_3$, $(Ba,Sr)TiO_3$, or $BaTi_{0.8}Zr_{0.2}O_3$. In a further aspect, the metal oxide comprises a quarternary metal oxide, for example, $Pb(Zr,Ti)O_3$.

[0098] In one aspect, the metal oxide nanoparticle can be selected from the group consisting of a titanate-based ferroelectric; a manganate-based material; a cuprate-based material; a tungsten bronze-type niobate, tantalate or titanate or a layer bismuth tantalate, niobate, or titanate; bismuth titanate; strontium bismuth tantalate; strontium bismuth niobate; strontium bismuth tantalate niobate; lead zirconate titanate; lead lanthanum zirconate titanate; lead titanate; bismuth titanate; lithium niobate; lithium tantalate; strontium rhuthenate; barium titanate; and strontium titanate and mixtures thereof.

[0099] In a further aspect, the metal oxide nanoparticle can be selected from the group consisting of $BaTiO_3$, $PbTiO_3$, and $SrTiO_3$ or the group consisting of $BaTiO_3$, $SrTiO_3$, and $BaTi_{0.8}Zr_{0.2}O_3$. In one aspect, the metal oxide nanoparticle comprises $BaTiO_3$.

[00100] In one aspect, suitable metal oxides, in the bulk, can have a ferroelectric phase. Also, in one aspect, suitable metal oxide nanoparticles can have a ferroelectric phase.

[00101] It is understood that the coated metal oxides of the invention can be selected to have a relatively large dielectric permittivity. For example, in one aspect, suitable metal oxides, in the bulk, can have a dielectric constant of greater than about 100, greater than

about 150, greater than about 200, greater than about 300, greater than about 500, or greater than about 1000. In a further aspect, suitable metal oxide nanoparticles can have a dielectric constant of greater than about 10, greater than about 20, greater than about 30, greater than about 40, greater than about 50, or greater than about 100.

2. PARTICLE SIZE

[00102] When referring to the particles size of nanoparticles used in connection with the invention, it is understood that the ranges refers to average particles size. Further, the particle size of a coated nanoparticle of the invention refers to the average particle size of the nanoparticle and coating.

[00103] Typically, the coated metal oxide nanoparticles used in connection with the invention can range in size between about 1 and about 100 nanometers, for example, between about 20 and about 500 nanometers, between about 49 and about 120 nanometers, between about 60 and about 100 nanometers, between about 100 and about 300 nanometers, between about 300 and about 500 nanometers, or between about 500 and about 1000 nanometers. In further aspects, the coated metal oxide nanoparticles used in connection with the invention can be provided at a particle size of less than about 1000 nanometers, for example, less than about 900 nanometers, less than about 800 nanometers, less than about 700 nanometers, less than about 600 nanometers, less than about 500 nanometers, less than about 400 nanometers, less than about 300 nanometers, less than about 200 nanometers, or less than about 100 nanometers.

3. LIGANDS

[00104] In one aspect, a coated metal oxide nanoparticle of the invention can comprise at least one phosphonic acid ligand. In a further aspect, a coated metal oxide nanoparticle of the invention can comprise a plurality of phosphonic acid ligands. In a further aspect, a coated metal oxide nanoparticle of the invention can comprise more than one type of phosphonic acid ligand; that is, the phosphonic acid ligands can have differing structures. In a yet further aspect, a coated metal oxide nanoparticle of the invention can be covered with phosphonic acid ligands.

[00105] The term "phosphonic acid ligand" as used herein refers to a radical or

residue attached to or capable of attaching to the surface of the metal oxide nanoparticles that is derived from a phosphonic acid. Those of ordinary skill in the art will understand that phosphonic acids or their anionic salts can be readily attached to a surface of a nanoparticle, by replacement of one or more of the oxygen atoms of the phosphonic acid with bonds ranging from covalent, to polar covalent, to ionic, and including through hydrogen bonding, between the phosphorus atom and an oxygen atom or ion on a metal oxide surface.

a. POLYMER-COMPATIBILIZING LIGANDS

[00106] It is known that phosphonic acids have a high affinity for metal oxide surfaces. Phosphonic-acid ligands have now been used to modify metal-oxide nanoparticles ($BaTiO_3$, $SrTiO_3$, $BaTi_{0.8}Zr_{0.2}O_3$) to give a high surface coverage (*ca.* 8 ligands nm^{-2}) as shown by elemental analysis and XPS. The surface-modifying agent is stable and is not removed upon washing with a variety of solvents including water, hexane and toluene, and the modified particles are still nanocrystalline according to XRD, TEM and SEM. The present modification technique is thus significantly more effective than the use of organosilanes to modify $BaTiO_3$ that has been reported in the scientific literature (*ca.* 1 ligand nm^{-2}).

[00107] Such modification allows us to prepare stable colloidal suspensions of these particles at high concentration (>1 mg mL^{-1}) in a wide range of solvents. The modified particles can be employed to give ceramic/polymer mixtures suitable for spin-coating from solution to form homogeneous films of thickness of from about 0.1 μm to about 5 μm (for example, from about 0.1 μm to about 3 μm or from about 0.1 μm to about 1 μm). Optimization of the compatibility of metal oxide particles can be achieved with specific polymer systems through the use of custom-synthesized phosphonic acids as outlined in Figure 1.

[00108] The disclosed phosphonic acid syntheses are straightforward, high-yielding (often 60% and above), and applicable to the formation of a wide variety of substituted ligands. For example, Figure 1 depicts ligands designed for compatibility with (a) alkyl- and fluoroalkyl-containing polymers (e.g., poly(vinylidenedifluoride)), (b) aromatic side-chain polymers (e.g., poly(styrene), poly(vinylcarbazole)), and (c) hydrophilic polymers

(e.g., poly(vinylalcohol)), along with (d) ligands that may be functionalized for compatibilization with tailor-made polymers through simple reaction of the alcohol or amine group. Further, polarizable groups such as C_{60} can be directly attached to the ceramic nanoparticles (Figure 1 (e)).

b. CROSS-LINKABLE GROUPS

[00109] Cross-linking between polymer chains can be a useful means of improving the mechanical strength of a material. Therefore, a range of phosphonic acids bearing functional groups that can be covalently bound to polymers by cross-linking reactions have been synthesized. This also entails the synthesis of custom-designed polymers with cross-linkable side chains compatible with the ligands on the nanoparticle surface. Ligands include phosphonic acids featuring both photo-cross-linkable groups, such as chalcones and cinnamate esters (Figure 2 (a)), and groups that can be cross-linked by ring-closing metathesis reactions (Figure 2 (b)). These ligands can be cross-linked to a polymer either before or after coating the ceramic particles.

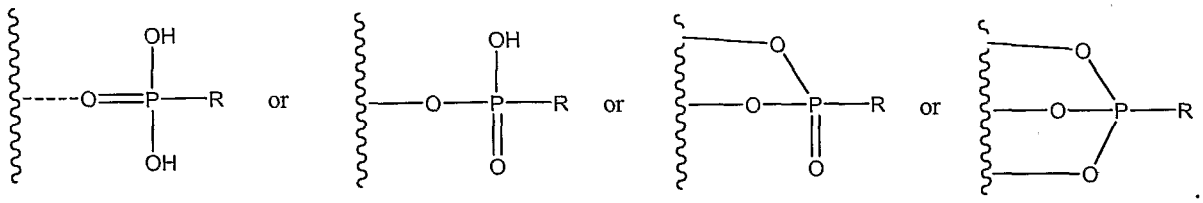
c. FUNCTIONALIZATION WITH POLYMERS

[00110] A further method to improve particle/polymer miscibility and, at the same time, increase the percentage ceramic loading by volume in the composite is to bind the polymer directly to the ceramic. This removes interfacial barriers inherent in the mixing of ceramic and polymer in solution and allows the formation of nanocomposites by simple melt or solution processing. Polymers can be directly bound to ceramic nanoparticles utilizing the disclosed phosphonic acid approach through the synthesis of suitably functionalized ligands. One strategy identified is to use phosphonic acids with polymerizable side-chains such as methacrylate and norbornene (Figure 3 (a)); these can be attached to the nanoparticles either pre- or post-polymerization. Another, potentially more powerful, approach is to employ the ring-opening metathesis polymerization (ROMP) reaction of functionalized strained alkenes to give polymers terminated with reactive groups that can be subsequently converted into phosphonic acids, affording well-defined polymer-functionalized phosphonic acids (Figure 3 (b)). Ring-opening metathesis polymerization reactions are well known and can be referenced in, for example, "Handbook of Metathesis," Grubbs (ed), Wiley, 2003.

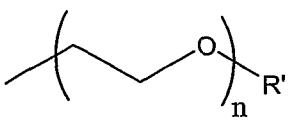
d. STRUCTURE

[00111] In certain aspects, the at least one organic phosphonic acid comprises *n*-octylphosphonic acid, methylphosphonic acid, 11-hydroxyundecylphosphonic acid, octadecylphosphonic acid, (11-phosphonoundecyl)phosphonic acid, (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phosphonic acid, benzylphosphonic acid, {2-[2-(2-methoxyethoxy)ethoxy]ethyl}phosphonic acid, [3-(4-{[4′-(phenyl-*m*-tolylamino)biphenyl-4-yl]-*m*-tolylamino}phenoxy)propyl]-phosphonic acid, (11-prop-2-ynyloxyundecyl)phosphonic acid, pentafluorobenzylphosphonic acid, pentabromobenzylphosphonic acid, (11-acryloyloxyundecyl)phosphonic acid, (11-cinnamoyloxyundecyl)phosphonic acid, 3-(9*H*-carbazol-9-yl)propylphosphonic acid, 3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)propylphosphonic acid, or pentabromobenzylphosphonic acid or a mixture thereof.

[00112] In one aspect, the phosphonic acid ligands are attached to the surface by bonds ranging from covalent, to polar covalent, to ionic, and including through hydrogen bonding, from one, two, or three of the oxygen atoms of the phosphonic acid ligands to the metal oxide surface. For example, the organic phosphonic acid ligands can be attached to the surface by covalent bonding as illustrated by one or more of the structures illustrated below:



[00113] In one aspect, R can be an organic radical comprising 1 to 18 carbon atoms, for example, an organic radical comprising 1 to 16 carbons, 1 to 14 carbons, 1 to 12 carbons, 1 to 10 carbons, 1 to 8 carbons, 1 to 6 carbons, or 1 to 4 carbons. In a further aspect, R is an alkyl substituted polyether having the structure:

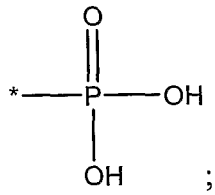


wherein n is 1 to 25 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19,

20, 21, 22, 23, 24, and 25), and R′ is a C1-C4 alkyl (including 1, 2, 3, or 4 carbons). In a yet further aspect, R is selected from methyl, ethyl propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl.

[00114] In a still further aspect, R is a residue of a polymer. For example, R can be a residue of epoxy resin, a polyimide resin, a cyanate ester or polyurethane, a polyvinylidene difluoride, a fluoropolymer, such as Teflon or Viton, a polyester, a polycarbonate, a polycarbonate-carbonate, a polyether-ketone, a polyphenylene oxide, or a polyphenylene sulfide, or copolymers thereof.

[00115] In one aspect, the phosphonic acid ligand can comprise a phosphonic acid compound comprising a residue of a compound having the structure G_n-R-X_n, wherein G is a terminal group; wherein R is a bridging group; wherein X is a phosphonic acid group having the structure:



; and

wherein each n is, independently, 1, 2, or 3. In a yet further aspect, each n is 1. In a still further aspect, the compound comprises the structure G-R-X.

e. TERMINAL GROUPS

[00116] In one aspect, the terminal group comprises an alkyl, a perfluoroalkyl, an aryl, a perfluroaryl, a hydroxyl, an amine, an amide, an ester, a thiol, a selenol, a phosphine, a phosphonic acid, or a phosphonate ester group.

[00117] In certain aspects, the terminal group can be one or more of a luminescent group, a polymerizable group, a cross-linkable group, or a coordinating group.

[00118] In a further aspect, the terminal group is a luminescent group. As used herein, the term "luminescent group" refers to a moiety that emits or is capable of emitting electromagnetic radiation, for example in fluorescent and/or phosphorescent processes. In one aspect, a luminescent group can emit absorbed electromagnetic radiation. In a further

aspect, the electromagnetic radiation can be emitted at a different wavelength than that at which it is absorbed. In a yet further aspect, the luminescent group can emit electromagnetic radiation in response to a stimulus, for example, in response to incident light. In a still further aspect, the terminal group is a luminescent group comprising an organic dye. While, in one aspect, the terminal group can be any luminescent group known to those of skill in the art, exemplary organic dyes include xanthene dyes (e.g., rhodamines, fluoresceins, and coumarins), cyanines, porphyrins, phthalocyanines, squaraines, croconiums, coronenes, perylene diimides, lumogens (BASF), and two-photon dyes such as A-π-A, D-π-D and A-π-D species where A represents an acceptor group, π represents a conjugated bridge and D represents a donor group.

[00119] In a further aspect, the terminal group is a polymerizable group. As used herein, the term "polymerizable group" refers to a moiety that participates or is capable of participating in a process of forming a polymeric species by combining relatively large numbers (>3) of chemical units or monomers into relatively longer linear or branched chains. The process can be, for example, a chain-growth or a step-growth polymerization process. Exemplary polymerization processes include radical, cationic, anionic, condensation polymerization, polyhomologation, metal-catalyzed-coupling-based polymerization, ring opening polymerization (ROP), and ring opening metathesis polymerization (ROMP). In one aspect, the polymerizable group can undergo a polymerization reaction in response to a stimulus, for example, a change in pH, the presence of an initiator or a catalyst, or in response to incident light.

[00120] Exemplary polymerizable groups include a vinyl, an allyl, a styryl, an acroyl, an epoxide, an oxetane, a cyclic-carbonate, a methacroyl, an acrylonitrile, an isocyanate, an isothiocyanate, or a strained ring olefin group.

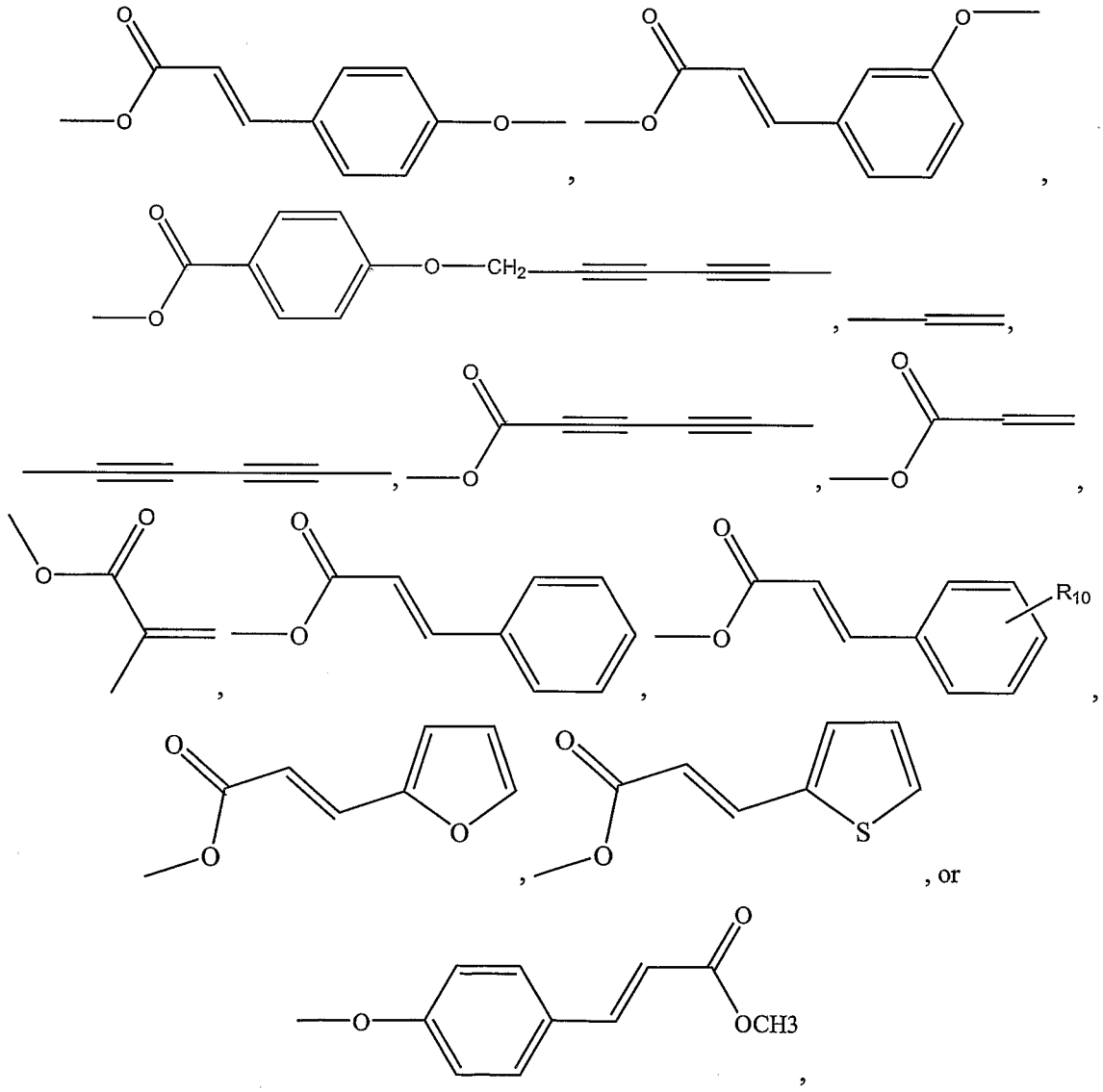
[00121] In a further aspect, the terminal group is a polymerizable group comprising a strained ring olefin group. Although the strained olefin can generally be any known to those of skill in the art of polymer chemistry, in one aspect, the polymerizable group is selected from dicyclopentadienyl, norbornyl, and cyclobutenyl.

[00122] In a further aspect, the terminal group is a polymerizable group comprising a silyl group, for example, $-(CH_2)\eta SiCl_3$, $-(CH_2)\eta Si(OCH_2CH_3)_3$, or $-(CH_2)\eta Si(OCH_3)^3$,

wherein η is an integer from 0 to 25. In further aspects, η is an integer from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or an integer from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00123] In a further aspect, the terminal group is a polarizable group. Exemplary polymerizable groups include *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine and C_{60}.

[00124] In a further aspect, the polymerizable group comprises a residue of



wherein R_{10} is a linear or branched alkyl group having up to 25 carbons. In various aspects, R_{10} can be a linear or branched alkyl group having from 1 to 25 carbons (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, and 25 carbons),

having up to 12 carbons (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 carbons) or having up to 8 carbons (including 1, 2, 3, 4, 5, 6, 7, and 8 carbons).

[00125] In a further aspect, the terminal group is a cross-linkable group. As used herein, the term "cross-linkable group" refers to a moiety that can engage in reactions and bond formation with moieties in the matrix or on other particles to form a three-dimensional network structure. In one aspect, a cross-linkable group can be a ligand or a polymer that, upon exposure to a stimulus, for example a radical initiator or temperature increase or ultraviolet light, forms a bond with a moiety in a matrix, substrate, polymer or another such ligand on another particle. In a further aspect, a cross-linkable group can participate in a process of forming a three-dimensional polymer network, in contrast to a simple linear polymer chain. In one aspect, the terminal group is a cross-linkable group comprising chalcone, cinnamate, vinyl, cyclooct-4-eneyl, alkyne, azide, succinimide, or maleimide.

[00126] In a further aspect, the terminal group is a coordinating group, for example a metal ion coordinating group. As used herein, the term "coordinating group" refers to a moiety that forms or is capable of forming coordination bonds with an inorganic species, for example, a cationic species. For example, the coordinating group can comprise a crown ether (including 12-crown-4, 15-crown-5, and 18-crown-6) or a cryptand, or a multidentate ligand, such as ethylenediaminetetraacetic acid.

f. BRIDGING GROUPS

[00127] In one aspect, R comprises a substituted or unsubstituted, linear or branched, C_3 to C_{50} aliphatic or cyclic aliphatic, fluoroalkyl, oligo(ethyleneglycol), aryl, or amino group. Although a bridging group can be independently selected for use in connection with the composition and methods of the invention, in a further aspect, a bridging group can be selected in combination with a terminal group.

[00128] For example, in one aspect, G is an amino group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta NR_{a2}R_{a3}$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha NR_{a2}R_{a3}$, $-(CF_2)_\beta CH_2NR_{a2}R_{a3}$, $-OCHCH_2-(CF_2)_\beta CH_2NR_{a2}R_{a3}$, or $-O(CF_2)_\beta CH_2NR_{a2}R_{a3}$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, and wherein R_{a2} and R_{a3} independently comprise H, a linear or branched alkyl group having up to 25 carbons. In various further aspects, R_{a2} and

R_{a3} can independently comprise linear or branched alkyl groups having up to 12 carbons (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 carbons) or having up to 8 carbons (including 1, 2, 3, 4, 5, 6, 7, and 8 carbons), and α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00129] In a further aspect, G is a halogen and R and G together comprise -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta$F, -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$Cl, -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$Br, -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$I, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$F, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Cl, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Br, or -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$I, wherein γ is an integer from 0 to 25, wherein δ is an integer from 0 to 25, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25. In various further aspects, α, β, δ, and γ can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00130] In a further aspect, G is a cyano group and R and G together comprise -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$CN or -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$CN, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25. In various further aspects, α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00131] In a further aspect, G is a aldehyde group and R and G together comprise -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$CHO or -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$CHO, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25. In various further aspects, α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

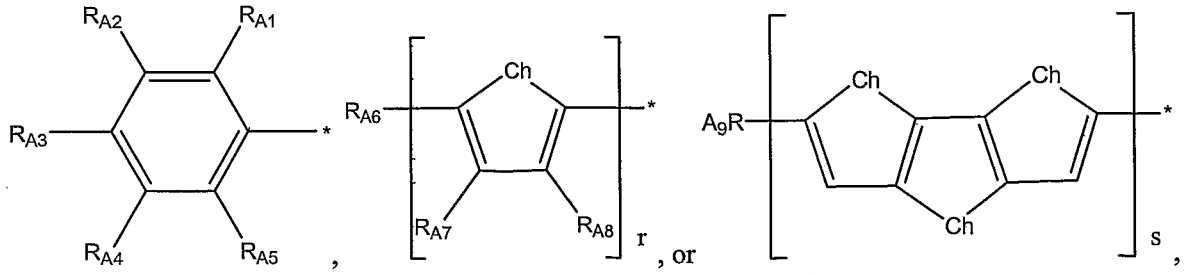
[00132] In a further aspect, G is a nitro group and R and G together comprise -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta NO_2$ or -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha NO_2$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein γ is an integer from 0 to 25, and wherein δ is an integer from 0 to 25. In various further aspects, α, β, δ, and γ can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00133] In a further aspect, G is an alkyl group and R and G together comprise -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta OR_{a1}$, -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$-CCH, -$(CH_2)_\beta$-$(CH_2CH_2O)_\alpha$-CCH, -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$-$CHCH_2$, -$(CH_2)_\beta$-$(CH_2CH_2O)_\alpha$-$CHCH_2$, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$-R_{a1}, -$(CF_2)_\beta OR_{a1}$, -$(CF_2)_\beta CF_3$, -$O(CF_2)_\beta OR_{a1}$, or -$OCHCH_2$-$(CF_2)_\beta$-OR_{a1}, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, and wherein R_{a1} comprises H, a linear or branched alkyl group having up to 25 carbons.

[00134] In various further aspects, R can comprise linear or branched alkyl groups having up to 12 carbons (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 carbons) or having up to 8 carbons (including 1, 2, 3, 4, 5, 6, 7, and 8 carbons), and α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00135] In a further aspect, G is a fluorinated group and R and G together comprise -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha F$, -$OCHCH_2$-$(CF_2)_\beta CF_3$, -$(CF_2CF_2)_\alpha$-$(CF_2)_\beta CF_3$, -$(CF_2)_\beta$-$(CF_2CF_2)_\alpha CF_3$, -$(CF_2CF_2)_\alpha$-$(CH_2)_\beta CF_3$, or -$(CF_2)_\beta$-$(CF_2CF_2)_\alpha CF_3$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25. In various further aspects, α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00136] In further aspects, G is an aromatic group and R and G together comprise -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$-Phenyl, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Phenyl, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Phenyl, -$(CF_2)_\beta$-$(OCH_2CH_2)_\alpha$Phenyl, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Aryl, -$(CF_2)_\beta$-$(OCH_2CH_2)_\alpha$Aryl, -$(OCH_2CH_2)_\alpha$-$(CF_2)_\beta$Aryl, -$(OCH_2CH_2)_\alpha$-$(CH_2)_\beta$Aryl, -$O(CH_2)_\beta$Aryl, or -O-$(CF_2)_\beta$Aryl, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein Aryl is



wherein Ch is Se, S, or O, wherein r is an integer from 0 to 50, wherein s is an integer from 0 to 3, and wherein R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, R_{A6}, R_{A7}, R_{A8}, and R_{A9} independently comprise

$-(CH_2CH_2O)_\gamma-(CH_2)_\delta OCH_3$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta N(CH_3)_3$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta CON(CH_3)_2$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta CN$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta F$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta NO_2$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta CHO$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta Cl$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta Br$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta I$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta$Phenyl, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma CH_3$, $-(CH_2)_\delta-(OCH_2CH_2)_\delta N(CH_3)_2$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma CON(CH_3)_2$, $-(CH_2)_\delta-(CH_2CH_2O)_\gamma CN$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma F$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma NO_2$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma CHO$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma Cl$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma Br$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma I$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma$Phenyl, $-(CF_2)_\beta OCH_3$, $-(CF_2)_\beta CH_2ON(CH_3)_2$, $-(CF_2)_\beta CF_3$, $-O(CF_2)_\beta OCH$, $-OCH_2CH_2-(CF_2)_\beta OCH$, $-OCH_2CH_2-(CF_2)_\beta CH_2N(CH_3)_2$, $-O(CF_2)_\beta CH_2N(CH_3)_2$, $OCH_2CH_2-(CF_2)_\beta CHO$, $-O(CF_2)_\beta CHO$, $-OCH_2CH_2-(CF_2)_\beta CF_3$, $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, or $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, wherein γ is an integer from 0 to 25, and wherein δ is an integer from 0 to 25. In various further aspects, α, β, δ, and γ can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8). In various further aspects, r can be an integer from 1 to 25 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, and 25), an integer from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or an integer from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8). In various further aspects, s can be 1, 2, or 3.

[00137] In a further aspect, G is an ionic group comprising SO_3^-, $-NR^{11}{}_3^+$, $-PO_3H^-$, $-PO_3^{2-}$, or $-COO^-$, wherein each R^{11} is independently selected from H or alkyl.

[00138] In a further aspect, G is a polymerizable group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-CH=CH_2$ or $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-CH=CH_2$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25. In various further aspects, α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00139] In a further aspect, G is a cross-linkable group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-C\equiv CH$, $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-C\equiv CH$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-N_3$, or $-(CH2)_\beta-(CH_2CH_2O)_\alpha-N_3$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25. In various further aspects, α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

[00140] In a further aspect, G is an amide group and R and G together comprise -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta CONR_{a2}R_{a3}$ or -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$ $CONR_{a2}R_{a3}$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein R_{a2} and R_{a3} independently comprise H, a linear or branched alkyl group having up to 25 carbons. In various further aspects, R_{a2} and R_{a3} can independently comprise linear or branched alkyl groups having up to 12 carbons (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 carbons) or having up to 8 carbons (including 1, 2, 3, 4, 5, 6, 7, and 8 carbons), and α and β can be, independently, integers from 1 to 12 (including 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12) or integers from 1 to 8 (including 1, 2, 3, 4, 5, 6, 7, and 8).

g. COATING

[00141] In one aspect, the phosphonic acid ligands form a coating on the surface of the metal oxide nanoparticle. As used herein, the term "coating" refers to a layer of a second material, for example ligands, attached to or contact with at least a portion of the surface of a first material, such as the surface of the metal oxide nanoparticles described herein. In one aspect, the coating substantially covers the surface, thereby providing a substantially complete monolayer of the coating material (such as the phosphonate ligands described herein). In a further aspect, the coating covers either substantially less or substantially more than the entire surface, forming sub-monolayer or multilayer coverage, respectively.

[00142] In one aspect, the phosphonic acid ligands sufficiently cover the metal oxide nanoparticle surface to form an approximately full monolayer on the metal oxide nanoparticle surface. In a further aspect, the organic phosphonic acid ligands are present in a concentration of at least about 2 ligands per nm^2 of metal oxide surface area, for example, at least about 2 ligands per nm^2, at least about 3 ligands per nm^2, at least about 4 ligands per nm^2, at least about 5 ligands per nm^2, at least about 6 ligands per nm^2, at least about 7 ligands per nm^2, at least about 8 ligands per nm^2, at least about 9 ligands per nm^2, at least about 10 ligands per nm^2, at least about 11 ligands per nm^2, at least about 12 ligands per nm^2.

[00143] In a further aspect, the phosphonic acid ligands are present in a concentration of from about 8 ligands per nm^2 of metal oxide surface to about 10 ligands per nm^2 of metal

oxide surface area. In yet further aspects, the phosphonic acid ligands are present in a concentration of from about 5 ligands per nm^2 to about 15 ligands per nm^2, of from about 5 ligands per nm^2 to about 10 ligands per nm^2, of from about 8 ligands per nm^2 to about 12 ligands per nm^2, of from about 5 ligands per nm^2 to about 12 ligands per nm^2, of from about 5 ligands per nm^2 to about 8 ligands per nm^2, or of from about 5 ligands per nm^2 to about 15 ligands per nm^2. In one aspect, the phosphonic acid ligands are present in a concentration of from about 8 ligands per nm^2 to about 10 ligands per nm^2 of metal oxide surface area.

[00144] The surface area can be either calculated by simple mathematics (using perfect spheres of known diameter as approximations of the nanoparticles) or experimentally measured by adsorption/desorption of inert gas. In one aspect, BET specific surface area methods can be used to calculate the surface area of the nanoparticles expressed in m^2/g. Thermogravimetric analysis (TGA) on both uncoated and coated nanoparticles can then be performed to determine the weight loss attributable to loss of attached ligands. Without wishing to be bound by theory, assuming that there is no change in the density of coated particle from that of uncoated particle, the weight loss per gram of particles is divided by the molecular weight of the ligand to calculate the number of ligands that were attached to gram of particles. This number can then be converted to the number of ligands per unit area. Elemental analysis (EA) and energy dispersive spectroscopy (EDS) results can also be used in similar way to calculate the coverage. In the literature, it is known that the footprint of phosphonic acid on a titanium dioxide surface is 0.24 nm^2, which corresponds to 4.2 ligands per nm^2.

C. METHODS FOR PREPARING COATED METAL OXIDE NANOPARTICLES

[00145] In one aspect, the coated metal oxide nanoparticles of the invention can be provided by the methods of the invention.

[00146] In a further aspect, a method for preparing the coated metal oxide nanoparticles of the invention comprises the steps of providing the metal oxide nanoparticles; and reacting the metal oxide nanoparticles with the phosphonic acid or an ester or salt thereof, so as to attach at least some of the phosphonic acid to the metal oxide nanoparticle surface, to form a coated metal oxide nanoparticle. In a further aspect, the methods of the invention can further comprise a step of isolating and purifying the coated

metal oxide nanoparticles. The step of providing the metal oxide nanoparticles can comprise, for example, a step of treating or etching the surface of the metal oxide nanoparticles to at least partially remove any surface contaminants thereon. Suitable etchants include aqueous NH_4Cl, aqueous HCl, and aqueous HNO_3. In on aspect, dilute acidic media, for example NH_4Cl aqueous solution, 0.1 N HCl, or 0.1 N HNO_3, can be used to remove $BaCO_3$ in the case of $BaTiO_3$ and can also promote the hydrolysis of surface groups to generate more hydroxyl groups on the surface, thereby enhancing surface coating.

[00147] In a further aspect, the methods can further comprise the steps of purification and isolation of the coated metal oxide nanoparticle.

[00148] In a yet further aspect, a method for preparing the coated metal oxide nanoparticle of the invention comprises the steps of treating a metal oxide nanoparticle with an etchant; and reacting the etched metal oxide nanoparticle with a phosphonic acid ligand having an anchoring group that can bind to the metal oxide nanoparticle. In one aspect, an anchoring group can comprise a phosphonic acid or phosphonate anion moiety.

D. NANOCOMPOSITE COMPOSITIONS

[00149] Generally, the coated metal oxide nanoparticles of the invention can be used to provide the nanocomposite compositions of the invention. In one aspect, a nanocomposite composition can comprise a polymer; and a plurality of coated metal oxide nanoparticles of the invention dispersed within the polymer. In a further aspect, the polymer has a dielectric constant greater than or equal to about 2.25 and less than about 100 (e.g., greater than or equal to about 2.25 and less than about 60 or greater than or equal to about 2.25 and less than about 30) when measured at 1 kHz.

1. POLYMERS

[00150] Generally, the polymer can be any polymer known to those of skill in the art of polymer chemistry. Suitable polymers include but are not limited to base polymer resins, and in particular epoxies, polyimides, and cyanate esters. Suitable epoxies include but are not limited to cycloaliphatic epoxy and bisphenol-A epoxy. Exemplary base polymer resins include but are not limited to: 3,4-epoxycyclohexylmethyl-(3,4-epoxy) cyclohexane carboxylate (sold under the trademarks ERL 4221 by Union Carbide Plastics Company or

Araldite CY 179 by Ciba Products Company); bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate (sold under the trademarks ERL 4289 by Union Carbide Plastics Company or Araldite CY 178 by Ciba Products Company); vinylcyclohexene dioxide (ERL 4206 made by Union Carbide Plastics Company); bis(2,3-epoxycyclopentyl)ether resins (sold under the trademark ERL 4205 by Union Carbide Plastics Company); 2-(3,4-epoxy) cyclohexyl-5,5-spiro (3,4-epoxy)-cyclohexane-m-dioxane (sold under the trademark Araldite CY 175 by Ciba Products Company); glycidyl ethers of polyphenol epoxy resins, such as liquid or solid bisphenol A diglycidyl ether epoxy resins (such as those sold under trademarks as Epon 826, Epon 828, Epon 830, Epon 1001, Epon 1002, Epon 1004, etc., by Shell Chemical Company); phenol-formaldehyde novolac polyglycidyl ether epoxy resins (such as those sold under the trademarks DEN 431, DEN 438, and DEN 439 by Dow Chemical Company); epoxy cresol novolacs (such as those sold under the trademarks ECN 1235, ECN 1273, ECN 1280 and ECN 1299 by Ciba Products Company); resorcinol glycidyl ether (such as ERE 1359 made by Ciba Products Company); tetraglycidyl tetraphenylethane (Epon 1031 made by Shell Chemical Company); glycidyl ester epoxy resins such as diglycidyl phthalate (ED-5661 by Celanese Resins Company); diglycidyl tetrahydrophthalate (Araldite CY 182 by Ciba Products Company) and diglycidyl hexahydrophthalate (Araldite CY 183 made by Ciba Products Company or ED-5662 made by Celanese Resins Company); and flame retardant epoxy resins such as halogen containing bisphenol A diglycidyl ether epoxy resins (e.g., DER 542 and DER 511 which have bromine contents of 44-48 and 18-20%, respectively, and DER 661 all of which are made by Dow Chemical Company). Epoxy resins suitable for use in the present invention are well known in the art and are set forth, for example, in many patents including U.S. Pat. Nos. 2,324,483; 2,444,333; 2,494,295; 2,500,600; and 2,511,913. Suitable polymers also include polyvinylidene difluoride, Viton, Polyesters (e.g., Mylar) - ester (K = 3.2 - 4.3)[Kapton - ether and imide], Polyamides (e.g., Nylon) - amide (K = 3.14 -3.75), Polycarbonate - carbonate (K = 2.9), [PEEK - ether and ketone], [Poly(phenylene oxide) - PPO - ether], [Poly(phenylene sulfide) - PPS- thioether], and Teflon AF.

[00151] In one aspect, the polymer is an epoxy, a polyimide, a cyanate ester or polyurethane, a polyvinylidene difluoride, a fluoropolymer such as Teflon or Viton, a polyester, a polycarbonate, a polycarbonate-carbonate, a polyether-ketone, a polyphenylene oxide, or a polyphenylene sulfide, a polyvinylphenol, polyvinylpyrrolidinone, polyolefin

(polyethylene and polypropylene), polyester (PET), polyethylene naphthalate (PEN), cyanoethylated pullulan and other pulluan esters, siloxane polymers, and copolymers of a vinylidenefluoride or a trifluoroethylene or a chlorotrifluoroethylene or a hexafluoropropylene or copolymers thereof or mixtures thereof.

[00152] In a further aspect, the polymer is a cross-linkable polymer. That is, the polymer is functionalized with one or more cross-linkable groups and can engage in reactions and bond formation with moieties in the matrix or on other particles to form a three-dimensional network structure. In one aspect, individual polymer chains can form crosslinks with other individual polymer chains within the composition. In a further aspect, individual polymer chains can form crosslinks with cross-linkable groups in the phosphonic acid ligands of the nanoparticles and/or nanocomposites of the invention.

[00153] In one aspect, the polymer is a crystalline polymer. In a further aspect, the polymer is a semi-crystalline polymer.

[00154] In a further aspect, the polymer is a polymer resin. As used herein, the term "resin" refers to solid or semi-solid organic products of natural or synthetic origin, generally of high (and often indeterminate) molecular weights with no definite melting point. A resin can include natural, synthetic, and natural/synthetic blends.

2. SOLVENTS

[00155] In a further aspect the polymer soluble in an organic solvent. It is understood that a polymer can be selected for its solubility or its insolubility in a selected solvent or solvent mixture; however, suitable polymers need not be soluble in all organic solvents. In a further aspect, a polymer can be selected for its insolubility or partial solubility in a selected solvent. Suitable organic solvents include N,N-dimethyl formamide (DMF), pyridine, N-methyl pyrrolidinone (NMP), chloroform, chlorobenzene, cyclohexane, methylehtyl ketone, methylisobutyl ketone, propyleneglycol methylether (PGME), propyleneglycol methylether acetate (PGMEA), o-xylene, decaline, or trichlorobenzene or mixtures thereof. In one aspect, the organic solvent is selected from the group consisting of tetrahydrofuran, acetonitrile, acetone, dimethylformamide, methanol, ethanol, and ethylene glycol and mixtures thereof.

[00156] In one aspect, the polymer soluble in a polar solvent, for example, water.

[00157] In a further aspect, a method for preparing a coated nanoparticle can comprise the steps of treating a metal oxide nanoparticle with an etchant; and reacting the etched metal oxide nanoparticle with a phosphonic acid ligand having an anchoring group that can bind to the metal oxide nanoparticle.

E. FILMS AND METHODS FOR PRODUCING FILMS

[00158] In one aspect, the nanocomposites of the invention can be used to provide films. In a further aspect, films can be prepared by the methods of the invention. In a yet further aspect, films can be provided from nanocomposites prepared by methods of the invention. In a still further aspect, articles can be prepared from the films of the invention.

[00159] In one aspect, the invention relates to a method for preparing a film comprising the steps of dispersing or dissolving the coated metal oxide nanoparticles of the invention in a solvent; dissolving a polymer in the solvent to form a solution or dispersion of the polymer and coated metal oxide nanoparticles; and forming a film comprising the nanocomposite. In a further aspect, the forming step comprises at least one of spin coating, doctor blading, spray coating, drop casting, meniscus coating, or dip coating the solution or dispersion on a substrate, and removing or allowing the evaporation of the solvent, to form the film on the substrate. In a yet further aspect, the forming step comprises screen printing, ink-jet printing, or other printing methods known in the art. In certain further aspects, the polymer is can be any of the disclosed polymers. In certain yet further aspects, the solvent can be any of the disclosed solvents.

F. APPLICATIONS

[00160] In one aspect, the compositions of the invention can find utility in a wide range of applications. For example, dispersions of ligand-coated metal oxide nanoparticles can be used in polymer matrices to form homogenous, high dielectric constant film materials. As another example, films of ligand coated metal oxide nanoparticles can be used in polymer matrices in capacitor applications, including high energy density capacitors.

[00161] As another example, ligand-coated metal oxide nanoparticles can be used

where the ligand contains a functional group that can be polymerized to afford a dispersion of metal oxide nanoparticles in polymer directly. In such an example, the metal oxide/polymer composite is thus formed from a single component, in the absence of any added polymer or polymer precursor.

[00162] As another example, ligand-coated metal oxide nanoparticles can be used where the ligand or mixture of ligand is bound directly to a polymer. As another example, ligand-coated metal oxide nanoparticles can be used where the ligand contains a functional group that can be bound to polymers directly either by photochemical or thermal reaction (e.g., cross-linking). This can enhance the mechanical strength of metal oxide/polymer composites. As another example, ligand-coated metal oxide nanoparticles can be used where the ligand contains a luminescent functional group for sensing applications. As another example, ligand coated metal oxide nanoparticle containing nanocomposites can be used as piezoelectric or ferroelectric materials. As another example, ligand coated metal oxide nanoparticle containing nanocomposites can be used as high dielectric or high refractive index materials in variety of optical and electronic applications including high energy density capacitors.

[00163] Generally, a capacitor is a device that stores energy in the electric field created between a pair of conductors on which electric charges have been placed. The capacitance value, or amount of charge that can be stored, is directly proportional to the permittivity of the dielectric material that separates the conductors of the capacitor. The coated metal oxide nanoparticles of the invention and/or the nanocomposites of the invention can allow the formation of high quality, defect free thin films that exhibit high dielectric constants. These thin films enable a greater amount of charge to be stored on a specific conductor, enabling the production of smaller, higher density capacitors. The high quality of the composite films can also result in less leakage current between the conductors, resulting in a more efficient capacitor.

[00164] In one aspect, the invention relates to a capacitor comprising at least one coated metal oxide nanoparticle of the invention. In a further aspect, the invention relates to a capacitor comprising a nanocomposite composition of the invention. In one aspect, the invention relates to a capacitor comprising the films of the invention. In a further aspect, the film comprises two or more layers of the nanocomposite composition of the invention.

Likewise, in a further aspect, capacitors can be produced by the methods of the invention.

[00165] In one aspect, the capacitor comprises a film having a dielectric constant of greater than about 19, for example, of greater than about 20, of greater than about 30, of greater than about 40, of greater than about 50, of greater than about 60, of greater than about 70, of greater than about 80, of greater than about 90, or of greater than about 100.

[00166] In a further aspect, the capacitor comprises a film having a dielectric breakdown strength of greater than about 120 V/micrometer, for example, of greater than about 130 V/μm, of greater than about 140 V/μm, of greater than about 150 V/μm, of greater than about 180 V/μm, or of greater than about 200 V/μm.

[00167] In a further aspect, the capacitor comprises a film having an energy density of greater than about 3 J/cm^3, for example, of greater than about 4 J/cm^3, of greater than about 5 J/cm^3, of greater than about 6 J/cm^3, of greater than about 7 J/cm^3, of greater than about 8 J/cm^3, of greater than about 9 J/cm^3, of greater than about 10 J/cm^3, of greater than about 15 J/cm^3, or of greater than about 20 J/cm^3.

[00168] In a further aspect, the capacitor comprises a film having a dielectric constant of greater than about 19, a dielectric breakdown strength of greater than about 120 V/micrometer, and an energy density of greater than about 3 J/cm^3.

G. EXAMPLES

[00169] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary and are not intended to limit the disclosure. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

1. PREPARATION OF COATED NANOPARTICLES

[00170] Nanopowders of barium titanate (BT) were obtained from Aldrich (diameter

~70 nm) whose crystal phase is determined to be cubic phase by X-ray powder diffraction. *n*-octylphosphonic acid (98%) was obtained from Alfa Aesar and octyltrimethoxysilane (96%), nonanoic acid (96%), 1-octylsulfonic acid sodium salt (98%) were obtained from Aldrich and used without further purification.

a. GENERAL EXEMPLARY NANOPARTICLE PREPARATION METHOD

[00171] Dispersion in 25 mL of 95:5 (v/v) ethanol:H_2O per gram $BaTiO_3$ (BT) was homogenized by ultrasonic processing followed by the addition of 0.5 mmol of phosphonic acid. The mixture was stirred at 80°C for 1 hr and 24 hr. Alternatively, the metal oxide nanoparticles can be coated with phosphonic acid by using microwave energy, rather than or in addition to heating. The nanoparticles were rinsed with excess ethanol by ultrasonication at 30 ~ 40 °C for 1 hour followed by centrifugation. The clear supernatant solution was decanted then the precipitated nanoparticles were redispersed and rinsed repeatedly by the same method. After washing, the nanoparticles were overnight dried under vacuum at 80°C.

[00172] Nanocomposite solutions were prepared by initially ball milling barium titanate nanoparticles in pyridine (Fluka) for PC (bisphenol A type polycarbonate, PolySciences) host and in N,N-dimethylformamide (Aldrich) for P(VDF-HFP) (Aldrich) host, then the polymers were added to the respective nanoparticle dispersions and further ball milled to yield stable dispersions.

[00173] Thin films of the nanocomposite were fabricated by spin coating the dispersions on an aluminum coated glass substrate as the base electrode. The aluminum surface was pretreated by cold plasma treatment with 3 SCFH (standard cubic feet per hour) air at 750W power for 10 minutes then stored in absolute ethanol before use to clean the surface and to promote the wetting of the nanocomposite dispersions. The thickness of the films after soft baking (110°C) was measured by a Tencor KLA P15 contact profilometer.

[00174] Parallel plate capacitors were fabricated by depositing the top electrodes on the dielectric nanocomposite thin films. 500 nm thick aluminum was deposited through a shadow mask by a thermal evaporator (Model PVD75, Kurt J. Lesker) at 3 Å/sec deposition rate. The mask has array of capacitors with circular electrodes of 0.5 mm and 1 mm diameter.

[00175] Frequency dependent capacitance and loss tangent (dissipation factor) using a parallel equivalent circuit were measured by an Agilent 4284A LCR meter from 20 Hz to 1 MHz at 1 VRMS applied voltage in open/short correction mode to eliminate the residual capacitance from the cables connected between the meter and the probe station. The final measurement was taken with "long" integration time and average reading from every four measurement. Leakage current density was measured by applying bias across the device up to 100 VDC while monitoring the current by an Agilent E5272A source/monitor unit. Dielectric breakdown strength was measured using a Keithley 248 high voltage supply by sweeping the applied voltage from 50 VDC at approximately 10 V/sec until the point of catastrophic device failure. For all of the different characterization experiments explained above instrument control and data collection were automated using LabVIEW software. All the electrical characterizations of the capacitor devices were measured in a humidity and oxygen controlled (> 0.1 ppm) glove box on a probe station (Signatone, model H100) with a blunt tungsten tip (Signatone, SE-T, 5.0 μm tip diameter, 25 mil. shank diameter) to minimize the mechanical damage to soft organic-containing films.

b. EXAMPLE 1

[00176] Surface pretreatment on BT nanopowders, which removes barium carbonate impurities and provides consistent surface conditions from batch to batch, was done as follows. 4 g of BT was dispersed in 95 mL of distilled water with 1.4 g of ammonium chloride (Fisher Scientific). The dispersion was ultrasonicated in order to remove barium carbonate impurity from BT. The dispersion was washed three times each with 100 mL of distilled water by ultrasonication and centrifugation, then dried in vacuum oven at 80 °C overnight.

[00177] For preparation of surface modified barium titanate (BT) nanoparticles, 0.4 g of $BaCO_3$-free BT was dispersed in 10 mL of 95:5 (v/v) mixture of absolute ethanol and distilled water (Solvent A) followed by ultrasonication for 6 hours to achieve better dispersion. 0.2 mmol of each ligand was dissolved in 1 mL of Solvent A and added to the dispersion of BT. The whole mixture was further ultrasonicated for 1 hour and stirred at 80 °C overnight. After the surface modification, BT nanopowders were washed three times each with 20 mL of absolute ethanol to remove any excess unbound ligands and dried in

100 °C oven for 1 hour. The dried powder was placed in a vacuum oven at 70 °C overnight to remove residual solvent. BT nanopowders before and after surface modification were characterized by FT-IR, XRD, SEM, EDS, solid-state NMR, TGA, and Elemental Analysis. The ligand is not removed by washing with a wide variety of solvents, including water, acetone, chloroform, hexanes, THF, and toluene, indicating strong and stable complexation to the metal oxide powder.

[00178] TGA analysis (Figure 4) of n-octylphosphonic acid modified $BaTiO_3$ nanoparticles shows that the composite loses ca 6% of its mass upon heating to 500 °C. Heating the sample afterwards in the same manner does not result in any significant mass loss, indicating that all the ligand has been removed. Unmodified $BaTiO_3$ nanoparticles do not have any significant mass loss in this temperature range. Quantitative analyses on the modified particles by EDS and elemental analysis resulted in 3.4 and 4.9 % ligand by weight, respectively. Without wishing to be bound by theory, assuming the size and shape of the $BaTiO_3$ particle are 70 nm in diameter and spherical with no significant change in its density before and after modification, the ligand coverages can be calculated as tabulated in Table 1 (Calculated ligand coverages of *n*-octylphosphonic acid-coated $BaTiO_3$ (70 nm in diameter) from various methods).

Table 1

Source of Data	No. of ligands per particle	No. of ligands per nm^2	Corresponding foot-print of n-OPA
EDS	118,000	7.7	13.1
EA	174,000	11.3	8.9
TGA	216,000	14.0	7.1

c. EXAMPLE 2

[00179] Surface modification of $BaTiO_3$ (70nm in diameter from Aldrich, 120nm in diameter from Nanoamorphous Inc., and 100nm in diameter from Inframat Advanced Materials Co.) nanoparticles by G-R-X type ligands, in which X is phosphonic acid was performed. 0.4 g of $BaTiO_3$ nanoparticles were dispersed in 10 mL of 95:5 (v/v) absolute ethanol:distilled water solvent mixture (Solvent A) and ultrasonicated for 6 hours. Each phosphonic acid ligand ca. 0.2 mmol, depending on its purity, was dissolved either

separately in 1 mL of Solvent A or directly in the dispersion of $BaTiO_3$ nanoparticles.

[00180] After adding the ligand (or ligand solution), the mixture was ultrasonicated for 1 hour and brought to 80 °C oil bath overnight with vigorous stirring by a magnetic spin bar at 1,000~1,500 rpm. The mixture was cooled to room temperature and washed thoroughly with plenty of absolute ethanol to remove unreacted excess ligands because all the phosphonic acid ligands used were readily soluble in ethanol. This was done by successive ultrasonication and centrifugation, in which the powder was redispersed in 20 mL ethanol by stirring followed by ultrasonication then the suspension was centrifuged at 3,000 rpm for 100 minutes.

[00181] The clear supernatant part was removed and the precipitated particles were redispersed in fresh 20 mL absolute ethanol for the next washing cycle. These washing cycles were repeated usually three to six times depending on the dispersability of the modified particles. When the powders were not sticky and easily sedimented by centrifugation, three washing cycles were used. For the powders which are sticky and not easily separated by centrifugation, up to six washing cycles were used to remove excess ligands. The phosphonic acid ligands used are tabulated in Table 2 and selected FT-IR spectra of coated $BaTiO_3$ nanoparticles are shown in Figure 5.

Table 2

Name of phosphonic acid ligand	Abbreviation
*n-Octylphosphonic acid	*OPA
*Methylphosphonic acid	*MPA
11-hydroxyundecylphosphonic acid	HUPA
Octadecylphosphonic acid	ODPA
(11-phosphonoundecyl)phosphonic acid	DPPA
(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phosphonic acid	FOPA
Benzylphosphonic acid	BZPA
{2-[2-(2-Methoxyethoxy)ethoxy]ethyl}phosphonic acid	PEGPA
[3-(4-{[4'-(Phenyl-*m*-tolylamino)biphenyl-4-yl]-*m*-tolylamino}phenoxy)propyl]-phosphonic acid	TPDPA
(11-Prop-2-ynyloxyundecyl)phosphonic acid	TKYNPA

*Commercially available; OPA from Alfa Aesar, 98%, MPA from Aldrich, 98%.

[00182] Engineering of the surface properties of metal oxide nanoparticles can be further extended by introducing blends or mixtures of different ligands on the same nanoparticle. Two different methods; i) coating of nanoparticle surface by a mixture of different ligands; ii) exchanging already-coated nanoparticle surface with different ligand were performed and selected results are shown in Figure 6. Exchange of OPA ligands coated on the BT surface with TPDPA was done by refluxing 100mL absolute ethanol dispersion of 0.2 g of OPA-coated BT with 3-times molar equivalent TPDPA at 100 ℃ for 1 hour.

[00183] ^{31}P Solid state NMR spectroscopy shows the presence of *n*-octadecylphosphonic acid; comparison with the free acid (in a direct polarization experiment) shows that there are two phosphonic acid species present in the nanocomposite, presumably surface-bound acid species (at lower ppm than the free acid) and loosely-associated acid molecules (broad peak at higher ppm). Cross-polarization experiments provide corroborating evidence for the peak at lower ppm being due to surface-bound species.

d. EXAMPLE 3

[00184] $BaTiO_3$ (100nm), $BaZr_{0.2}Ti_{0.8}O_3$ (200nm) and $SrTiO_3$ (100nm) nanoparticles were obtained from Inframat Advanced Materials Co. and treated with n-octylphosphonic acid (Alfa Aesar, 98%) by methods similar to those previously described. Figures 7 and 8 show that the methodology is applicable to metal oxide nanoparticles in general, and that modification does not alter the morphology of the particles.

e. EXAMPLE 4

[00185] 0.2 g of $BaTiO_3$ (70nm, Aldrich) nanoparticles were dispersed in 10mL of Solvent A by ultrasonication for 6 hours. Added to this dispersion was 0.069 g of TPDPA then, the mixture was further ultrasonicated for 1 hour followed by stirring at 80 °C overnight. The coated nanoparticles were washed five times by ultrasonication and centrifugation each time with 20mL absolute ethanol. The white final product was dried in 100 °C oven for 1 hour, then dried under vacuum at 80 °C overnight. TPDPA-coated

nanoparticles showed strong blue fluorescence under UV lamp. The product was characterized by FT-IR, UV-VIS absorption, fluorescence emission and excitation experiments.

[00186] In order to remove excess unbound or loosely bound TPDPA, coated nanoparticles were Soxhlet extracted in absolute ethanol for 10 days. The extraction solvent was fluorescent after extraction. This may be due to washed TPDPA from the particle or due to loss of some surface-bound TPDPA. However, TPDPA-coated $BaTiO_3$ nanoparticles were still strongly fluorescent after such a harsh washing condition (see Figure 9).

[00187] Figures 9 and 10 indicate the presence of the TPD group in the composite, and demonstrate the introduction of functionality to metal oxide nanoparticles by treating with suitable organic ligands.

f. EXAMPLE 5

[00188] Surface modified nanoparticles can form more stable dispersions than unmodified nanoparticles in particular organic solvents depending on their functionalities on the surface. For example, dispersions of $BaTiO_3$ nanoparticles coated with *n*-octylphosphonic acid showed enhanced long-term stability in ethanol, chloroform, acetone, and N-methylpyrrolidinone (NMP) compared to the dispersions of unmodified $BaTiO_3$ nanoparticles. Nanocomposite solutions were prepared by dispersing coated nanoparticles in polymeric matrices. 50:50 (v/v) PEGPA-coated $BaTiO_3$ nanoparticles and polycarbonate (PolyScience, cat. No. 0962, Lot No. 00584) were dispersed in dioxane. The mixture was ultrasonicated to completely dissolve polymer and disperse nanoparticles until forming highly viscous creamy solution. Nanoparticles coated with mixed ligands can be also used to form a stable dispersion with polymeric matrix. 50:50 (v/v) nanoparticle:polymer composite was prepared in dimethylformamide (DMF) from poly(vinylidenefluoride)-co-poly(hexafluoropropylene) (aka. Viton, from Aldrich) and $BaTiO_3$ nanoparticles coated with 1:1 mixture of OPA and FOPA ligands. Thin films for capacitor applications were fabricated by spin coating nanocomposite solutions on cold plasma treated aluminum/glass substrate. The films were thermally annealed and characterized by optical microscope, AFM, SEM, and surface profilometers.

2. EXEMPLARY PHOSPHONIC ACID COMPOUND SYNTHESES

[00189] A generalized synthesis is represented by the Arbuzov reaction of the respective alkyl halide with $P(OEt)_3$ followed by hydrolysis (see, e.g., Figure 11). The Arbuzov reaction can be accelerated, if desired, by use of microwave irradiation.

a. 3-(4-{[4'-(PHENYL-*M*-TOLYLAMINO)BIPHENYL-4-YL]-*M*-TOLYLAMINO}PHENOXY)PROPYL]-PHOSPHONIC ACID DIETHYL ESTER

[00190] [3-(4-{[4'-(Phenyl-*m*-tolylamino)biphenyl-4-yl]-*m*-tolylamino}phenoxy)]propylbromide (0.75 g, 1.15 mmol), Al_2O_3 (neutral, Grade 1, 1.5 g) and $P(OEt)_3$ (5 ml, excess) were placed in a 50 ml RBF fitted with a reflux condenser. The mixture was subjected to microwave irradiation (300 W) for 3 hours (max. temp *ca.* 155 °C) after which time the starting bromide was no longer visible by TLC. Volatiles were distilled *in vacuo* (150 °C, 0.01 torr) to give the crude material as a thick yellow oil. Column chromatography (silica gel, EtOAc elution) afforded the desired product as a glassy, pale yellow solid. Yield 0.52 g, 64 %. Analysis found (calculated) %: C 75.56 (76.03), H 6.77 (6.66), N 3.98 (3.94). ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 7.38 (m, 4H), 7.20-6.95 (m, 16H), 6.84 (t, J = 7 Hz, 1H), 6.71 (d, J = 9 Hz, 4H), 3.91 (m, 4H), 3.57 (t, J = 6 Hz, 2H), 2.03 (s, 3H), 1.99 (s, 3H), 1.95 (m, 2H), 1.78 (m, 2H), 1.03 (t, J = 7 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 298 K): δ 155.93, 148.64, 148.47, 148.31, 147.82, 147.27, 141.37, 139.31, 139.18, 135.42, 134.45, 129.56, 129.54, 129.46, 128.12, 127.89, 127.57, 125.61, 124.63, 124.53, 124.18, 123.51, 123.34, 122.88, 122.27, 121.21, 115.79, 67.78 (d, $J_{C\text{-}P}$ = 16 Hz), 61.24 (d, $J_{C\text{-}P}$ = 6 Hz), 23.16 (d, $J_{C\text{-}P}$ = 5 Hz), 22.86 (d, $J_{C\text{-}P}$ = 142 Hz), 21.37, 21.27, 16.52 (d, $J_{C\text{-}P}$ = 6 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz, 298 K): δ 31.72. MS (ESI, m/z): 710 (M^+, 40 %).

b. [3-(4-{[4'-(PHENYL-*M*-TOLYLAMINO)BIPHENYL-4-YL]-*M*-TOLYLAMINO}PHENOXY)PROPYL]- PHOSPHONIC ACID MONOSODIUM SALT

[00191] [3-(4-{[4'-(Phenyl-*m*-tolylamino)biphenyl-4-yl]-*m*-tolylamino}phenoxy)propyl]-phosphonic acid diethyl ester (0.50 g, 0.7 mmol) was dissolved in CH_2Cl_2 (20 ml) under N_2. Bromotrimethylsilane (0.2 ml, 1.6 mmol) was added *via* syringe and the mixture was stirred for 2 hours. Volatiles were removed *in vacuo* to give a

glassy, pale-yellow solid; this was dissolved in methanol (MeOH) (50 ml) with fuming to give a clear solution. The mixture was stirred for 4 hours overnight and evaporated to dryness to give a pale yellow powder. ^{1}H NMR spectroscopy indicated incomplete hydrolysis, so the powder was redissolved in dry CH_2Cl_2 (10 ml) under N_2 and stirred overnight in the presence of bromotrimethylsilane (0.4 ml, 3.2 mmol). After removal of volatiles *in vacuo* and further MeOH hydrolysis the mixture was evaporated to dryness and a pale yellow powder was obtained. This was recrystallized from ethanol (EtOH) to give the product as an orange-pink powder; elemental analysis of the recrystallized material was consistent with the monosodium salt. Yield 0.36 g, 0.6 mmol, 79 %. Analysis found %: C 72.67 (72.77), H 5.89 (5.66), N 4.15 (4.14). ^{1}H NMR (d_6-DMSO, 400 MHz, 298 K): δ 7.50 (t, J = 9 Hz, 4H), 7.29 (t, J = 8 Hz, 2H), 7.17 (d of t, J = 8 Hz, J = 8 Hz, 2H), 7.04-6.98 (m, 7 Hz, 7H), 6.92 (d, J = 9 Hz, 4H), 6.88-6.77 (m, 6H), 3.99 (t, J = 6 Hz, 2H), 2.21 (s, 3H), 2.20 (s, 3H), 1.88 (m, 2H), 1.65 (m, 2H). ^{13}C{^{1}H} NMR (d_6-DMSO, 100 MHz, 298 K): δ 155.40, 147.43, 147.24, 147.14, 146.81, 146.19, 139.84, 138.96, 138.73, 133.85, 132.64, 129.57, 129.46, 129.29, 127.41, 127.04, 127.01, 124.68, 124.10, 123.90, 123.54, 123.51, 123.28, 122.98, 121.97, 121.42, 120.25, 115.66, 67.74 (d, $J_{C\text{-}P}$ = 17 Hz), 24.09 (d, $J_{C\text{-}P}$ = 137 Hz), 22.98 (d, $J_{C\text{-}P}$ = 4 Hz), 21.12, 21.07. ^{31}P{^{1}H} NMR (d_6-DMSO, 162 MHz, 298 K): δ 27.01. MS (FAB, m/z): 654 ($M(diacid)^+$, 90 %). Exact mass found (calculated for $[M(diacid)+H]^+$, m/z): 654.26102 (654.26475). CV (0.1 M ^{n}Bu$_4$PF$_6$ / CH_2Cl_2, 298K, *vs.* FcH^+/FcH): + 0.24 V, + 0.49 V (both reversible).

c. (3,3,4,4,5,5,6,6,7,7,8,8,8-TRIDECAFLUOROOCTYL)PHOSPHONIC ACID DIETHYL ESTER

[00192] 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooctane (5.68 g, 11.98 mmol) and $P(OEt)_3$ (4 ml, excess) were placed in a 50 ml RBF fitted with a reflux condenser. The mixture was subjected to microwave irradiation (300 W) for 2 hours (max. temp *ca.* 155 °C) after which time the starting iodide was no longer visible by TLC. Volatiles were distilled *in vacuo* (150 °C, 0.01 torr) to give the crude material as a thick yellow oil. Column chromatography (silica gel, EtOAc elution) afforded the desired product as a thick pale yellow oil. Yield 3.71 g, 64 %. Analysis found (calculated) %: C 29.25 (29.77), H 2.96 (2.91). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 4.11 (m, 4H), 2.36 (m, 2H), 1.98 (m, 2H), 1.33 (t, J = 7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, 298 K): δ 121-105 (m, C-F coupling

unresolved), 62.18 (d, J_{C-P} = 6 Hz), 25.15 (t, J_{C-F} = 24 Hz), 17.10 (d of t, J_{C-P} = 148 Hz, J_{C-F} = 4 Hz), 16.34 (d, J_{C-P} = 6 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz, 298 K): δ 28.96. MS (FAB, m/z): 485 ($[M+H]^+$, 100 %). Exact mass found (calculated for $[M+H]^+$, m/z): 485.05499 (485.05513).

d. (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)phosphonic acid

[00193] (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)phosphonic acid diethyl ester (0.79 g, 1.6 mmol) was dissolved in CH_2Cl_2 (5 ml) under N_2. Bromotrimethylsilane (0.8 ml, 6.1 mmol) was added *via* syringe and the mixture was stirred for 6 hours. Volatiles were removed *in vacuo* to give a thick orange oil; this was dissolved in MeOH (20 ml) with fuming to give a yellow solution. The mixture was stirred overnight and evaporated to dryness to give a pale yellow powder. Addition of MeCN caused separation of a white solid from the yellow solution. The solid was collected by filtration, affording the desired product as a white powder. Yield 0.56 g, 1.3 mmol, 82 %. Analysis found (calculated) %: C 22.35 (22.45), H 1.25 (1.41). ^{1}H NMR (d_6-DMSO, 400 MHz, 298 K): δ 2.35 (m, 2H), 1.73 (m, 2H). $^{13}C\{^{1}H\}$ NMR (d_6-DMSO, 100 MHz, 298 K): δ 121-105 (m, C-F coupling unresolved), 25.13 (t, J_{C-F} = 23 Hz), 17.10 (d, J_{C-P} = 138 Hz). $^{31}P\{^{1}H\}$ NMR (d_6-DMSO, 162 MHz, 298 K): δ 22.87. MS (FAB, m/z): 429 ($[M+H]^+$, 100 %).

e. {2-[2-(2-Methoxyethoxy)ethoxy]ethyl}phosphonic acid diethyl ester

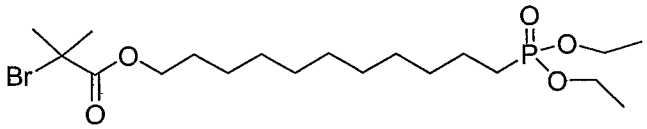
[00194] {2-[2-(2-Methoxyethoxy)ethoxy]ethyl}iodide (6.64 g, 24.3 mmol) and $P(OEt)_3$ (4.22 ml, 24.3 mmol) were dissolved in 1,4-dioxane (30 ml) and stirred under reflux for 24 hours. Volatiles were distilled *in vacuo* (150 °C, 0.01 torr) to give the crude material as a thick yellow oil. Column chromatography (silica gel, EtOAc:MeOH 95:5 elution) afforded the desired product as a pale yellow oil. Yield 1.0 g, 15 %. Alternative synthesis using {2-[2-(2-Methoxyethoxy)ethoxy]ethyl}iodide (5.00 g, 18.2 mmol) and $P(OEt)_3$ (10 ml, excess) under microwave irradiation (100 W, 1hr) gave higher yield after column chromatography (3.06 g, 10.7 mmol, 59 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ 4.08 (m, 4H), 3.67 (d of t, J_{H-P} = 10 Hz, J_{H-H} = 7 Hz, 2H), 3.60 (m, 6H), 3.50 (m, 2H), 3.36 (s, 3H), 2.09 (d of t, J_{H-P} = 20 Hz, J_{H-H} = 7 Hz, 2H), 1.28 (t, J = 7 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): δ 71.72, 70.35, 70.30, 69.97, 64.92, 61.44 (d, J_{C-P} = 6 Hz),

58.82, 26.77 (d, $J_{C\text{-}P}$ = 138 Hz), 16.22 (d, $J_{C\text{-}P}$ = 6 Hz). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz, 298 K): δ 29.23. MS (FAB, m/z): 285 ($[M+H]^+$, 100 %). Exact mass found (calculated for $[M+H]^+$, m/z): 285.15395 (285.14670).

f. {2-[2-(2-Methoxyethoxy)ethoxy]ethyl}phosphonic acid

[00195] {2-[2-(2-Methoxyethoxy)ethoxy]ethyl}phosphonic acid diethyl ester (1.00 g, 3.5 mmol) was dissolved in CH_2Cl_2 (20 ml) under N_2. Bromotrimethylsilane (2.3 ml, 17.5 mmol) was added *via* syringe and the mixture was stirred for 2 hours. Volatiles were removed *in vacuo* to give a thick orange oil; this was dissolved in MeOH (100 ml) with fuming to give a give a yellow solution. The mixture was stirred for 2 hours and evaporated to dryness to give a thick yellow oil which was dissolved in CH_2Cl_2 and extracted with NaOH (3 x 50 ml, aq., 1M). HCl (conc.) was added to the yellow aqueous layer until the solution was acidic to pH paper. Removal of water *in vacuo* gave a yellow crystalline solid that was extracted with EtOH and filtered. Cooling the filtrate to -35 °C resulted in precipitation of further white solid which was removed by filtration. Removal of volatiles from the yellow supernatant under vacuum (0.01 torr) afforded the desired product as a thick yellow oil. Yield 0.60 g, 2.6 mmol, 74 %. ^{1}H NMR (d_6-DMSO, 400 MHz, 298 K): δ 3.55 (ap. q. J = 7 Hz, 2H), 3.48 (m, 6H), 3.41 (m, 2H), 3.23 (s, 3H), 1.83 (d of t, $J_{H\text{-}P}$ = 19 Hz, $J_{H\text{-}H}$ = 7 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (d_6-DMSO, 100 MHz, 298 K): δ 71.25, 69.69, 69.58, 69.27, 65.41, 58.05, 28.99 (d, $J_{C\text{-}P}$ = 132 Hz). $^{31}P\{^{1}H\}$ NMR (d_6-DMSO, 162 MHz, 298 K): δ 23.15. MS (ESI, m/z): 227 ($^{44-}$, 100 %), 229 ($[M+H]^+$, 10 %). Exact mass found (calculated for $[M+H]^+$, m/z): 229.08490 (229.08410).

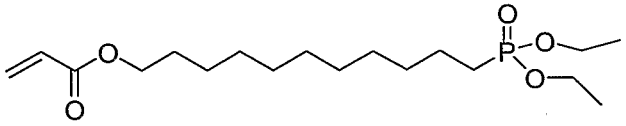
g. 2-Bromo-2-methyl-propionic acid 11-(diethoxy-phosphoryl)-undecyl ester



[00196] Diethyl 11-hydroxyundecylphosphonate (1.00 g, 3.24 mmol) and triethylamine (0.328 g, 3.24 mmol) were dissolved in ~20 mL dry DCM in a 50 mL rbf under argon. This mixture was stirred and put in an ice bath. Bromo-isobutyryl bromide (0.719 g, 3.56 mmol) was added dropwise via syringe. After 3.5 hours a thin layer

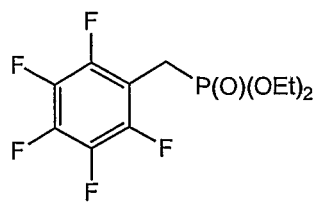
chromatogram (tlc) was taken in ethyl acetate. A column was run in ethyl acetate and the after removal of the solvent the desired compound was obtained as an orange oil (1.050 g, 75% yield). Analysis found (calculated) %: C 47.56 (47.65), H 7.98 (7.86).

h. 11-(DIETHOXYPHOSPHORYL)UNDECYL ACRYLATE



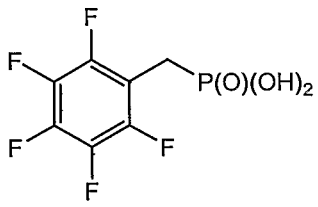
[00197] Diethyl 11-hydroxyundecylphosphonate (1.00 g, 3.24 mmol), triethylamine (0.328 g, 3.24 mmol) and a spatula tip of hydroquinone were dissolved in ~20 mL dry DCM in a 50 mL rbf under argon. This mixture was stirred and put in an ice bath. Acryloyl chloride (0.322 g, 3.56 mmol) was added dropwise via syringe. After 3 hours tlc of reaction mixture showed no starting material (ethyl acetate, I_2 stain). Reaction was stopped and toluene was added to the reaction mixture. The organic was washed with water and then dried and concentrated by rotary evaporation. The product was then redissolved in DCM and extracted with water. The organic was then dried and concentrated by rotary evaporation to yield a yellow oil. Upon high vacuum crystals started to form. The oil was then redissolved in acetonitrile and the crystals filtered. ^{1}H NMR of the crystals showed an unknown chemical species. The oil was concentrated by rotary evaporation and put on high vacuum again. The desired product was obtained as a yellow oil (444 mg, 38% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.40 (dd, J=17.32, 1.54 Hz), 6.12 (dd, J=17.32, 10.40 Hz), 5.81 (dd, J=10.36, 1.54 Hz), 4.17 - 4.02 (m, 4H), 4.14 (t, J=6.75 Hz, 2H), 1.80 – 1.50 (m, 6H), 1.42 – 1.22 (m, 20H). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$) δ 166.55, 130.66, 128.88, 64.91, 61.61 (d, J=6.88 Hz, 2C), 30.82 (d, J=17.21 Hz), 29.69 (2C), 29.55, 29.44, 29.31, 28.84, 26.13, 25.89 (d, J=139.97 Hz), 22.62 (d, J=4.59 Hz), 16.71 (d, J=5.74 Hz, 2C). Analysis found (calculated) %: C 58.66 (59.65), H 9.63 (9.73).

i. DIETHYL PERFLUOROBENZYLPHOSPHONATE



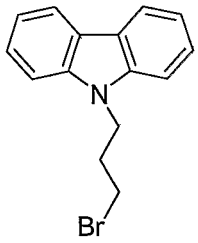
[00198] Perfluorobenzyl bromide (2.00 g, 7.66 mmol) and $P(OEt)_3$ (1.66 g, 9.96 mmol) were dissolved in 1,4-dioxane (10 ml) and heated at reflux for 14 hours. Fractional distillation (66-78 °C, 60 mm Hg) afforded the product as a colorless oil (2.43 g, 96 %)

j. PERFLUOROBENZYLPHOSPHONIC ACID



[00199] Diethyl perfluorobenzylphosphonate (1.90 g, 5.97 mmol) was dissolved in dry CH_2Cl_2 (4 ml), stirred and TMSBr (3.66 g, 23.88 mmol) was added. The mixture was stirred for 2 hours at room temperature after which volatiles were removed on a rotary evaporator to give a thick yellow oil. MeOH (5 ml) was added and the suspension stirred for 90 minutes, after which the product was collected by filtration yielding white crystals (1.20 g, 77 %).

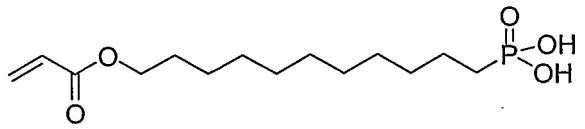
k. 9-(3-BROMOPROPYL)-9*H*-CARBAZOLE



[00200] Carbazole (15.00 g, 89.71 mmol) and 1,3-dibromopropane (45.5 mL, 450 mmol) were dissolved in ~200 mL dry THF and stirred under argon in a 500 mL rbf. Sodium hydride (3.23 g, 134.56 mmol) was added and the mixture was brought to reflux (~78° C) and allowed to do so for 40 hours. After cooling the mixture was diluted in ~800 mL water and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate and concentrated by rotary evaporation to leave an orange oil and light brown solid. This was distilled under high vacuum (0.05 Torr) at 100° C for 2 hours to remove excess dibromo compound. A tlc in 30:1 hexanes:ethyl acetate showed 6 spots. A column was run in 30:1 hexanes:ethyl acetate and the third spot was isolated as a thick yellow oil. This oil was dissolved in hot ethanol and put in the -20° C freezer overnight to yield a white solid

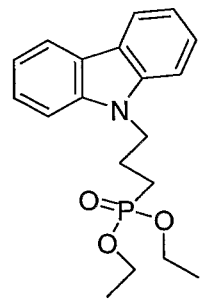
(7.70 g, 30% yield). This compound is reported in the literature and the ^{1}H NMR is consistent with the structure.

l. 11-(ACRYLOYLOXY)UNDECYLPHOSPHONIC ACID



[00201] 11-(diethoxyphosphoryl)undecyl acrylate (420 mg, 1.16 mmol) was dissolved in ~5 mL dry DCM. TMS bromide (0.33 mL, 2.55 mmol) was added via syringe and the rbf was greased and capped and allowed to stir for 2 hours. The solvent was concentrated by rotary evaporation and the product mixture redissolved in ~3 mL methanol and ~5 mL water and stirred for 2.5 hours during which a white precipitate formed. 1 M HCl was added and the product was extracted into dichloromethane, dried over magnesium sulfate, and pumped dry. The yellow/brown solid was dissolved in hot acetonitrile and put in the freezer overnight. Filtration afforded a white solid (143 mg, 40% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (br, s, 2H), 6.40 (dd, J=17.32, 1.61 Hz), 6.12 (dd, J=17.32, 10.41 Hz), 5.81 (dd, J=10.40, 1.60 Hz), 4.15 (t, J=6.73 Hz, 2H), 1.82 – 1.50 (m, 6H), 1.42 – 1.18 (m, 14H). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 166.76, 130.85, 129.05, 65.12, 30.87 (d, J=17.38 Hz), 29.89, 29.88, 29.76, 29.65, 29.46, 29.01, 26.33, 25.76 (d, J=143.86 Hz), 22.45 (d, J=4.85 Hz). Analysis found (calculated) %: C 55.09 (54.89), H 8.79 (8.88). ^{31}P{^{1}H} NMR (161.97 MHz, $CDCl_3$): δ 38.76.

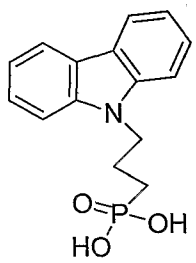
m. DIETHYL 3-(9H-CARBAZOL-9-YL)PROPYLPHOSPHONATE



[00202] Triethylphosphite (13.4 mL, 80.1 mmol) was added via syringe to 9-(3-bromopropyl)-9*H*-carbazole (7.70 g, 26.7 mmol) in a 50 mL rbf. The reaction was heated and stirred under Argon at 130° C for 18 hours. Excess triethylphosphite and side-products

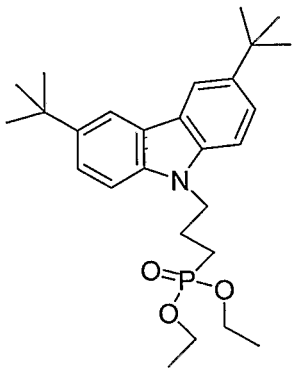
were removed under vacuum at ~100° C to yield a thick yellow oil (8.50 g, 92 % yield). ^{1}H NMR (400.14 MHz, CD_2Cl_2) δ 8.10 (dt, J=7.73, 2.00 Hz, 2H), 7.50-7.44 (m, 4H), 7.27-7.19, m, 2H), 4.43 (t, J=7.00 Hz, 2H), 4.10-3.95 (m, 4H), 2.23-2.09 (m, 2H), 1.74 (dt, J=18.41, 7.80 Hz, 2H), 1.26 (t, J=7.00 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100.62 MHz, CD_2Cl_2) δ 139.99 (2C), 125.36 (2C), 122.42 (2C), 119.88 (2C), 118.56 (2C), 108.37 (2C), 61.18 (d, J=6.44 Hz), 42.52 (d, J=15.39 Hz), 22.59 (d, J=141.97 Hz), 21.75 (J=4.83 Hz), 15.91 (d, J=5.84 Hz). $^{31}P\{^{1}H\}$ NMR (161.97 MHz, CD_2Cl_2): δ 31.22. Analysis found (calculated) %: C 65.67 (66.07), H 7.01 (7.00), N 4.05 (4.06). MS (EI, m/z): 290 ([M], 100 %). Exact mass found (calculated for [M], m/z): 345.14264 (345.14938).

n. 3-(9H-CARBAZOL-9-YL)PROPYLPHOSPHONIC ACID



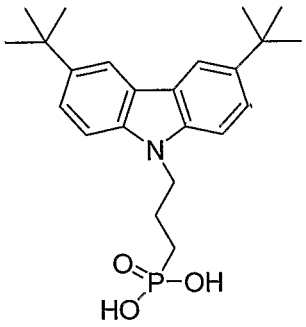
[00203] Trimethylsilyl(TMS)-bromide (1.12 mL, 8.67 mmol) was added via syringe to a solution of diethyl 3-(9H-carbazol-9-yl)propylphosphonate (1.00 g, 2.89 mmol) in ~20 mL dry DCM in a 50 mL rbf. The flask was greased and capped and allowed to stir for 90 minutes. The volatile organics were removed under vacuum and 30 mL of 1:1 MeOH:H_2O were added. The solution turned a cloudy whitish/grey. The solvents were removed and the product recrystallized from 2:1 H_2O:acetone (grey powder, 612 mg) and 1:1 H_2O:MeOH (PJH-II-5c, glassy grey solid, 42 mg). Both recrystallization solvents yielded pure product. Total yield was 78 %. ^{1}H NMR (400.14 MHz, DMSO) δ 8.15 (d, J=8.00 Hz, 2H), 7.65 (d, J=8.00 Hz, 2H), 7.45 (dt, J=15.41, 1.00 Hz, 2H), 7.19 (t, J=14.81 Hz, 2H), 4.48 (t, J=13.60 Hz, 2H), 2.03 – 1.89 (m, 2H), 1.59 – 1.46 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100.62 MHz, DMSO) δ 140.01 (2C), 125.76 (2C), 122.07 (2C), 120.33 (2C), 118.78 (2C), 108.33 (2C), 42.48 (d, J=17.31 Hz), 25.00 (d, J=137.35 Hz), 22.67 (d, J=4.13 Hz). $^{31}P\{^{1}H\}$ NMR (161.97 MHz, DMSO): δ 26.78. Analysis found (calculated) %: C 62.27 (62.28), H 5.56 (5.58), N 4.73 (4.84). MS (FAB, m/z): 290 ($[M+H]^+$, 100 %). Exact mass found (calculated for $[M+H]^+$, m/z): 290.09405 (290.09461).

o. DIETHYL 3-(3,6-DI-TERT-BUTYL-9H-CARBAZOL-9-YL)PROPYLPHOSPHONATE



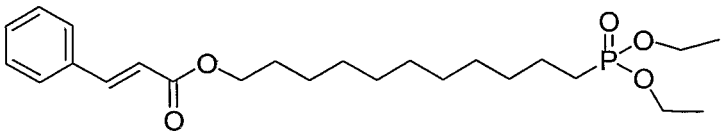
[00204] Diethyl 3-(9H-carbazol-9-yl)propylphosphonate (1.00 g, 2.89 mmol) was dissolved in 2-chloro-2-methylpropane (5.0 mL) and flushed with N_2 for 5 minutes. To this stirred solution was added aluminum chloride (1.16 g, 8.67 mmol) slowly. The solution turned chunky and black with gas bubbles appearing. The reaction was allowed to stir for 25 minutes after adding all the aluminum chloride. It was then quenched with 25 mL water and an extraction performed with water washings followed by 2 X 20 mL 1 M NaOH washings, then another water washing. The yellow organic layer was kept and dried and the solvent removed under vacuum. A tlc in ethyl acetate showed 4 spots with the brightest (and desired product) being the third spot from the top. A long column was run and the desired product was obtained as a thick yellow oil (447 mg, 34 % yield). ^{1}H NMR (400.14 MHz, CD_2Cl_2) δ 8.10 (d, J=1.6 Hz, 2H), 7.52 (dd, J=8.80, 2.00 Hz, 2H), 7.35 (d, 8.40 Hz, 2H), 4.36 (t, J=7.00 Hz, 2H), 4.08 – 3.93 (m, 4H), 2.21 – 2.07 (m, 2H), 1.71 (dt, J=18.14 Hz, 6.00 Hz, 2H), 1.45 (18H), 1.25 (t, J=7.00 Hz, 6H). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2) δ 142.14 (2C), 139.26 (2C), 123.80 (2C), 123.06 (2C), 116.68 (2C), 108.50 (2C), 61.89 (d, J=6.4 Hz, 2C), 43.36 (d, J=15.8 Hz), 34.92 (2C), 32.19 (6C), 23.35 (d, 142.2 Hz), 22.59 (d, J=4.9 Hz), 16.64 (d, J=5.8 Hz, 2C). ^{31}P{^{1}H} NMR (161.97 MHz, CD_2Cl_2): δ 31.34.

p. DIETHYL 3-(3,6-DI-TERT-BUTYL-9H-CARBAZOL-9-YL)PROPYLPHOSPHONIC ACID



[00205] Diethyl 3-(3,6-di-tert-butyl-9H-carbazol-9-yl)propylphosphonate (420 mg, 0.92 mmol) was dissolved in dichloromethane (10 mL) and sitrred. Bromotrimethylsilane (0.36 mL, 2.75 mmol) was added via syringe. The solution turned dark purple upon addition of the TMSBr. The round bottom was then capped with a greased glass stopper and allowed to stir for 2 hours. The solvent was pumped off and the mixture redissolved in a MeOH/DCM 1:1 mixture and allowed to stir for 2 more hours. Product was pumped down and then redissolved in MeOH/H_2O and pumped down again. 165 mg of a grey solid was isolated (45% yield). Alternatively, acetonitrile was used in a later reaction to clean/recrystallize the compound to yield a beige solid. ^{1}H NMR (400.14 MHz, DMSO) δ 8.17 (2H), 7.52-7.45 (m, 4H), 4.39 (t, J=6.67 Hz, 2H), 2.00-1.86 (m, 2H), 1.53-1.43 (m, 2H), 1.40 (18H). ^{13}C{^{1}H} NMR (125.77 MHz, DMSO) δ 140.97 (2C), 138.53 (2C), 123.18 (2C), 122.00 (2C), 116.34 (2C), 108.60 (2C), 42.51 (d, J=17.36 Hz), 34.41 (2C), 31.92 (6C), 25.07 (d, 137.22 Hz), 22.73 (d, J=4.02 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, DMSO): δ 26.79. Analysis found (calculated) %: C 65.87 (68.81), H 7.98 (8.03), N 3.35 (3.49). MS (ESI, m/z): 402 ([M+H]$^+$, 78 %). Exact mass found (calculated for [M+H]$^+$, m/z): 402.220000 (402.219259).

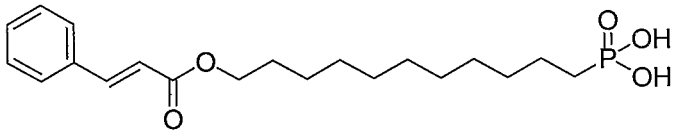
q. 11-(DIETHOXYPHOSPHORYL)UNDECYL CINNAMATE



[00206] The diethyl 11-hydroxyundecylphosphonate (1.00 g, 3.24 mmol) was combined with TEA (0.48 mL, 3.40 mmol) in 15 mL dry DCM in a 50 mL round-bottomed

flask (rbf) and the mixture was brought down to 0 °C. Cinnamoyl chloride (566 mg, 3.40 mmol) was added dropwise. The reaction was stirred for 2 hours and then stopped once most of the starting phosphonate was consumed. TLC in ethyl acetate showed several new spots. The reaction mixture was then washed 3X (20 mL) NaOH followed by sodium thiosulfate and water washes. The organic layer was then dried over magnesium sulfate and the solvent removed. A chromatography column in ethyl acetate was run and the desired product was isolated as a yellow-tinted oil with R_f= 0.60 (580 mg, 41% yield). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ 7.68 (d, J=16.02 Hz), 7.53 (m, 2H), 7.38 (m, 3H), 6.44 (d, J=16.02 Hz), 4.20 (t, J=6.74 Hz, 2H), 4.08 (m, 4H), 1.79-1.49 (m, 6H), 1.43-1.22 (m, 20H). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$) δ 167.02, 144.48, 134.39, 130.14, 128.79 (2C), 127.97 (2C), 118.21, 64.65, 61.28 (d, J=6.54 Hz, 2C), 30.54 (d, J=16.94), 29.42 (2C), 29.28, 29.20, 29.02, 28.65, 25.90, 25.62 (d, J=140.40 Hz), 22.33 (d, J=5.21 Hz), 16.42 (d, J=5.92 Hz, 2C). ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$): δ 33.32. Analysis found (calculated) %: C 65.39 (65.73), H 9.05 (8.96). MS (ESI, m/z): 439 ($[M+H]^+$, 100 %). Exact mass found (calculated for $[M+H]^+$, m/z): 439.25720 (439.26079).

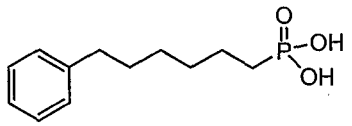
r. (*E*)-11-(CINNAMOYLOXY)UNDECYLPHOSPHONIC ACID



[00207] 11-(diethoxyphosphoryl)undecyl cinnamate (545 mg, 1.24 mmol) was dissolved in dry DCM (15 mL) in a 50 mL rbf and stirred. TMSBr (609 mg, 3.98 mmol) was added via syringe. The flask was greased and capped and allowed to stir for 90 minutes. The volatile organics were removed under vacuum and 20 mL of 1:3 MeOH:H_2O were added. The solvents were removed and the product recrystallized from acetonitrile (white crystalline solid, 425 mg, 90% yield). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.70 (m, 2H), 7.63 (d, J=16.00 Hz), 7.41 (m, 3H), 6.62 (d, J=16.00 Hz), 4.12 (t, J=6.50 Hz, 2H), 1.66-1.57 (m, 2H), 1.51-1.38 (m, 4H), 1.37-1.18 (m, 14H). ^{13}C{^{1}H} NMR (125.76 MHz, DMSO) δ 166.25, 144.38, 134.01, 130.44, 128.90 (2C), 128.34 (2C), 118.12, 64.03, 30.09 (d, J=15.94 Hz), 28.97, 28.95, 28.88, 28.71, 28.69, 28.21, 27.54 (d, J=136.52), 25.43, 22.73 (d, J=4.65 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, DMSO): δ 27.72. Analysis found (calculated) %: C 62.51 (62.81), H 8.21 (8.17). MS (ESI): Exact mass found (calculated for $[M+H]^+$,

m/z):383.197378 (383.198189).

s. 6-PHENYLHEXYLPHOSPHONIC ACID



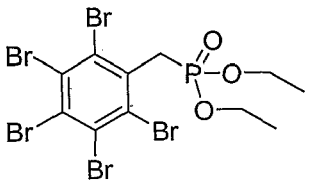
[00208] A dry 1 L round bottom flask, with a stir bar, was fitted with a schlenk adapter (the joints were greased) and put under vacuum. It was then filled with nitrogen and this cycle was repeated several times. To this round bottom was added ether (~500 mL) with a cannula. The iodobenzene (15 g, 0.0735 mol) was then added via syringe. Then the system was cooled to -78° C and n-butyl lithium (30 mL, 2.5M in hexane) was added via syringe. The system was then allowed to stir for 45 minutes under nitrogen pressure. A second system, prepared exactly as the first was set up alongside the first. Dry ether (~100 mL) was added followed by addition of an excess of 1,6-dibromohexane (53.8 g, 0.2025 mol). This was then cooled to -78° C but the dibromide froze so a 0 °C bath was used instead. The phenyl lithium complex was then transferred via cannula from the first to the second round bottom at a fast drop-wise rate. The second system was then fitted with a glass stopper and allowed to warm to room temperature and stir overnight. The final solution was a pale yellow color. Removal of the ether left an orange liquid with white precipitate. An extraction with hexanes and water was performed and the hexanes layer showed desired product via GC-MS. The hexane was then concentrated by rotary evaporation off. A distillation was run and the last fraction to come off was found to be 85 % for desired product by GCMS. This was purified no further and used as was in the next step.

[00209] The 1-bromo-6-phenylhexane (~7.304 g, ~30 mmol) from the previous step was then added to triethyl phosphite (25 mL, 143.7 mmol) in a round bottom flask fixed with a condenser and under Argon pressure. This was allowed to reflux overnight. GCMS (PJH-I-37b) showed no starting bromide left and the reaction was stopped. A distillation was performed to remove the excess triethyl phosphate and then a column in 2:1 hexane: ethyl acetate. The desired product had an $R_f = 0.55$. The desired product was obtained with only a trace impurity of the bisphenyl substituted hexane. The product was be purified further as it is a new compound, but some of it was used in the next step.

[00210] 6-phenyl hexylphosphonate (2.00 g, 6.71 mmol) was dissolved in20 mL of

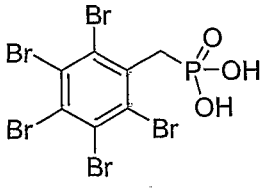
dry DCM in a 50 mL round bottom flask. To this was added TMS bromide (3.05 mL, 23.49 mmol) and the flask was capped with a grease stopper and allowed to stir for 2 hours. The flask was then concentrated by rotary evaporation to remove DCM and methanol was added and this was again allowed to stir, for 1 hour. The methanol was removed via rotovap and the product, 6-phenyl hexylphosphonic acid, was recrystallized from acetonitrile (6 different batches were obtained) for an overall yield of 1.294 g (79.7 %). ^{1}H NMR (300 MHz, DMSO) δ 7.28-7.10 (m, 5H), 2.54 (t, J=7.64 Hz, 2H), 1.60-1.15 (m, 10H). ^{13}C{^{1}H} NMR (125.77 MHz, $CDCl_3$) δ 142.59, 128.36 (2H), 128.24 (2H), 125.62, 35.80, 31.13, 30.205 (d, J=8.18 Hz), 28.63, 25.075 (d, J=144.63 Hz), 21.905 (d, J=1.89 Hz). Anal. Calcd for $C_{12}H_{19}PO_3$: C, 59.50; H, 7.91. Found: C, 59.64; H, 7.93.

t. DIETHYL PENTABROMOBENZYLPHOSPHONATE



[00211] Pentabromobenzylbromide (4.50 g, 7.96 mmol) was combined with triethylphosphite (4.36 g, 26.3 mmol) in a 25 mL rbf and was heated at 135° C for 15 hours. A solid precipitated upon cooling and was filtered and washed with hexanes (PJH-II-49a, beige powder, 4.237 g, 85% yield) ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 4.16-4.10 (m, 4H), 4.01 (d, J=22.5 Hz, 2H), 1.32 (t, J=7.00 Hz, 6H). ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$): δ 22.76.

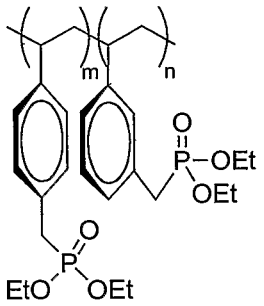
u. PENTABROMOBENZYL PHOSPHONIC ACID



[00212] Diethyl pentabromobenzylphosphonate (4.00 g, 6.42 mmol) was dissolved in dry DCM (20 mL) in a 50 mL rbf and stirred. TMSBr (3.44 g, 22.5 mmol) was added via syringe. The flask was greased and capped and allowed to stir for 4 hours. The volatile organics were removed under vacuum and 25 mL of MeOH was added and this was heated

at 85° C for 4 hours. A precipitate formed upon cooling and this was filtered and washed with acetonitrile (PJH-II-51e, white powder, 3.19 g, 88% yield). ^{1}H NMR (400.14 MHz, DMSO) δ 3.77 (d, J=21.72 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, DMF) δ 139.10, 129.09 (d, J=3.90 Hz, 2C), 128.33 (d, J=6.64 Hz, 2C), 127.11, 42.87 (d, J=130.5 Hz). $^{31}P\{^{1}H\}$ NMR (161.97 MHz, DMSO): δ 17.59.

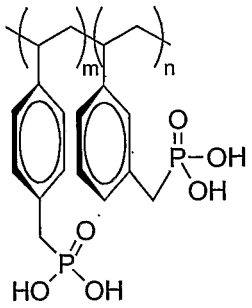
v. POLY(VINYLBENZYL PHOSPHONATE)



m/n=40/60
random co-polymer

[00213] Poly(vinylbenzyl chloride) (3.00 g, 19.7 mmol) was combined with triethylphosphite (9.8 g, 59 mmol) in a 25 mL round bottom flask and heated at reflux at 135 °C for 20 hours. The reaction mixture was a clear viscous liquid after cooling. Dichloromethane (DCM) was added to the product and this solution was then dripped into hexane to yield a white semi-solid/precipitate. The resulting precipitate was redissolved into DCM and dripped again into hexane. The precipitate was then dried and washed with ether (2 X 60 mL). The precipitate was redissolved again into DCM and precipitated into hexane again. The solvent was then removed via vacuum to remove a white sticky/glassy solid.

W. POLY(VINYLBENZYL PHOSPHONIC ACID)



m/n=40/60
random co-polymer

[00214] Poly(vinylbenzyl phosphate) (2.00 g, 7.87 mmol) was dissolved into dry DCM (15 mL) in a 50 mL round bottom flask. To this was added bromotrimethylsilane (3.01 g, 19.7 mmol) and the flask was capped with a greased cap and allowed to stir for 2 hours. The solvent was removed via rotovap and methanol (30 mL) was added and the flask was capped with a septum and allowed to stir for 90 minutes. The solvent was removed via vacuum leaving a pink crystalline solid in 102% yield (1.586 g). The greater-than-100% observed yield can be attributed to the unknown impurity peaks in the ^{1}H NMR.

3. PREPARATION, ANALYSIS, AND USE OF NANOCOMPOSITE FILMS

[00215] Nanocomposite solutions of both unmodified and surface modified barium titanate with PVP (poly(4-vinylphenol)) were prepared, and thin films from these materials were fabricated for use as capacitor dielectric materials.

a. BT:PVP COMPOSITE THIN FILMS

[00216] PVP (poly(4-vinylphenol)) composites of unmodified and PEGPA-modified BT were prepared and used to fabricate thin films for capacitors. A 10% PVP solution in 1-butanol was prepared by using 75:25:5 wt. % of PVP, hexamethoxymethylmelamine (Cymel 300), and Ts-H (p-toluenesulfonic acid) (Figure 12).

[00217] The mixture was cured at 150 °C for 3 hours to give a dark brown solid. Gravimetric analysis of the solid material indicated that the solid, after curing, contained 89.74% of its original solid content. From this result, 1:9 wt % BT:PVP composite solutions were prepared. ITO/glass substrates (15 Ω/cm^2) were cleaned by ultrasonication

in the following successive solutions: soap and tap water (15 min), distilled deionized water (15 min), acetone (15 min), ispropanol:ethanol 3:1 (15 min). The substrates were then dried in an 80 °C vacuum oven for at least 2 hours to remove residual solvent. Thin films of the BT:PVP composite were fabricated by passing the homogenized solution through a 1 μm syringe filter and spin coating at 2,000 and 4,000 r.p.m. Soft baking and subsequent curing of the PVP resin was done under the following condition: 25 °C to 100 °C ramping for 2 hr, soft bake at 100 °C for 3 hr, 100 °C to 150 °C ramping for 2 hr, followed by curing at 150 °C for 3 hr, and then 150 °C to 25 °C cooling for 5 hr. Top aluminum electrodes were deposited on the cured films through a shadow mask using an e-beam evaporator. Capacitances were measured using an Agilent 4284A LCR meter and the leakage currents were measured by current-voltage curves under varying applied bias up to 60 V by an Agilent E5272A two-channel source/monitor unit. Initial results showed dielectric constants (at 1 kHz) of 4.4~6.1 and 5.1~9.3 from unmodified BT:PVP and PEGPA-BT:PVP, respectively. All of the devices showed no significant leakage current under an applied bias of up to 60 V.

b. TGA RESULTS OF SURFACE-MODIFIED BT NANOPARTICLES

[00218] Thermogravimetric analysis (TGA) of octylphosphonic acid, octyltrimethoxysilane, nonanoic acid, and octylsulfonic acid salt coated BT nanoparticles was performed on a TA 2950 Thermogravimetric Analyzer. Observed weight loss percentages were in good agreement with FT-IR results. TGA was performed using 10~15 mg samples on a platinum crucible under air with the following temperature program: ambient temperature, ramping 10 °C/min to 900 °C, holding for 30 min (Figure 13).

[00219] Figure 14 shows the TGA of n-OPA coated on "as received" BT nanoparticles. Comparing from the result in Figure 2, the amount of coated phosphonic acid decreased from ~6 wt. % to ~2.8 wt. %, possibly due to leaching of Ba^{2+} ions during the NH_4Cl washing, resulting in the loss of Ba^{2+} binding sites and making the surface of BT more Ti-rich.

[00220] While not wishing to be bound by theory, it is believed that the surface binding mechanisms of carboxylic acids and phosphonic acids on BT surface are different. The former mainly involves coordination from electronegative oxygen on carboxylic group

to electron deficient Ba^{2+} while the latter involves both coordination from phosphonic acid to Ba^{2+} and condensation between hydroxyl groups from $-PO(OH)_2$ and Ti-OH.

[00221] Figure 15 shows the thermogravimetric profile of BTs coated with various phosphonic acids, representing the weight losses in agreement with the molecular weight of the respective phosphonic acid ligands used. The molecular weights of n-OPA, PEGPA, and pentafluorobenzylphosphonic acid (PFBZPA) are 194, 228, and 262, respectively. The molecular weight of P(VBPA) (poly(vinylbenzylphosphonic acid)) is not known, but is expected to be greater than small molecular phosphonic acids as it showed greater weight loss than any other phosphonic acid-coated BTs.

[00222] The FT-IR spectrum of PFBZPA modified BT indicated the presence of some unwashed $BaCO_3$ and the TGA showed corresponding high temperature burning species above 400 °C. To compare surface binding strengths, modifications should be made from the same starting point, *i.e.* from surface pre-treated BTs in all cases.

[00223] The weight loss profile of P(VBPA)-BT varies from that of other phosphonic acid-coated BTs, exhibiting a rapid decrease in total weight at low temperature and implying the presence of more volatile components. Figure 16 compares the TGA of P(VBPA) and P(VBPA)-BT, where there is rapid loss of weight in P(VBPA) at low temperature, potentially due to incompletely dried solvent molecules entrapped or bound to the non-surface bound free phosphonic acids. The weight loss around 450 °C can be attributed to the degradation of P(VBPA) as observed from the TGA of P(VBPA)-BT. The decomposition temperature of P(VBPA) is slightly higher than other phosphonic acids (~350 °C), indicating better thermal stability.

[00224] The various samples were characterized as BT:PVP thin films on ITO/glass (see Figure 17).

c. Formation of Films - PEGPA-BT in PC and PFBZPA-BT in Viton

[00225] 25, 50, and 75% bare BT and PFBZPA-BT filled Viton/dimethylformamide (DMF) sols were prepared and homogenized by magnetic stirring. PFBZPA-BT:Viton/DMF sol appears to show time-dependent rheological behavior with homogenization time. The initial state was a creamy viscous sol which appeared to be

strongly shear-thinning after some agitation period. The viscosity of the sol then suddenly dropped, forming a "grainy" sol, and behaved relatively weakly shear-thinning. The former state yielded good films while the latter did not when spin coated at 1,000 r.p.m. on untreated Al/glass. Bare-BT:Viton/DMF with high solid content (i.e., less DMF added) did not yield a good dispersion for spin coating.

[00226] BT:PC sols in pyridine did not yield good films, except for very highly filled sols because of the rapid evaporation rate of pyridine. Sols made from pyridine did exhibit low viscosity, indicating that DMF is a good dispersant. Films cast by doctor blade on Al/glass, and subsequently cold plasma treated and placed under air for 1 day were poor in quality due to rapid evaporation and were prone to delamination. Since the PC film and the PEGPA-BT are typically hydrophilic, cold plasma treatment immediately before the film fabrication can improve film fabrication.

d. DEVICE FABRICATION AND CHARACTERIZATION RESULTS

[00227] PFBZPA-BT:Viton/DMF with 50% and 75% vol. of filler with high solid content were used to fabricate 7~10 μm thick uniform films. The substrates were Cu electrode prepared by thermal evaporation on RCA cleaned glass slide with a 10 nm Cr adhesion layer, and Al/glass purchased from Newport Thin Film Laboratory (Chino, CA). Substrates were used without cold plasma treatment and the spinning speed was 400 r.p.m. for the initial spread of material and 1,000~1,500 r.p.m. for thinning the film. Due to the rectangular shape of the substrate, the turbulent air flow on the substrate perturbed the uniformity of the film. However, when a larger area substrate was used, there was enough uniform film area for device fabrication. Although the films had no defects when observed under X500 optical microscope, capacitance values measured from 50% and 75% BT films were only 9.8 and 11.4, respectively. SEM images of a 75% filled film showed many cracks on the surface and many voids and delamination on the cross-sections. Sedimentation was not observed across the film, which showed the dispersion was stable enough for fabrication of "initially" uniform and good wet films. Drying of the films was carried out under ambient air for a couple of days, followed by drying at 120 °C for 1 day, then vacuum drying at 80 °C for 2 days. Proper drying conditions typically provide superior results. While not wishing to be bound by theory, it is believed that the theoretical percolation threshold for ideally spherical particles is approximately 74% by volume. The BT here was truncated

cubic, with a percolation threshold higher than 74%, although cracks and voids may be difficult to avoid in 75% filled films. See, generally, Figure 18.

[00228] Other devices fabricated were also tested and the results are (at 1 kHz): 34.5 (3-layer 50% PFBZPABT:Viton, 1.92 μm), 72.8 (3-layer 50% PFBZPABT:Viton, 1.33 μm), 34.5 (3-layer bare-BT:Viton, 2.39 μm), 47.0 (2-layer PEGPABT:PC, 0.63 μm, not very clean data), 26.3 (4-layer PEG2PABT:PC, 0.85 μm), 36.8 (4-layer PEG2PA:BT, 1.27μm, non-uniform thickness), 24.2 (75% PEGPABT:PC, 4.28 μm), 10.1 (50% bare-BT:p(HEMA), 5.63 μm), and 13.6 (50% bare-BT:p(HEMA), 4.49μm). Some devices initially failed to show capacitance response, but worked well after vacuum drying at 80 °C for 2 days, implying that at least some portion of trapped and high boiling solvent molecules and/or adsorbed water molecules were present and affecting to the measurement.

e. EXAMPLE 9

[00229] Barium titanate nanoparticles (BT-8), approximately 200 nm, were obtained from Cabot Corporation. Dispersing media was 11.5:1.75 (wt.) mixture of PGMEA (propyleneglycol methylether acetate) and BYK-w-9010, a polymeric phosphate ester (Dow Chemical). 13.25 g of the resulting solvent and dispersant mixture was mixed with 55 g of BT in a 150 mL HDPE bottle. The mixture was ball-milled overnight by a bench-top roller in the presence of zirconia beads (~1 mm) and alumina chips (~10 mm). The dispersion was then spin coated at 2000~3000 r.p.m. on 3 in. x 2 in. rectangular Cu-coated glass slide with Ti adhesion layer prepared by DC sputtering. The quality of the film was not thoroughly investigated but appeared very homogeneous and uniform with no visible defects. About 30 circular top Cu electrodes (diameter ~1 mm) were sputtered through a shadow mask on top of the dielectric film. Thickness of the films was measured by contact profilometer and ranged was from a few to a few ten micrometers depending on the solid content.

f. USE OF COMMERCIAL DISPERSANT FOR $BaTiO_3$ DISPERSION

[00230] The addition of commercial dispersant BYK-W-9010 (BYK Chemie GmbH, ~2 wt. % to filler) increased the stability of $BaTiO_3$ dispersions. BYK-W-9010 is a co-polymer with many acidic groups made by esterification of a mixture of long aliphatic

alcohols and phosphoric acid. The non-esterified phosphoric acid groups can bind on the surface of $BaTiO_3$ and give both steric and electrostatic repulsive force to hold the nanoparticles apart in a suspension. Approximately 3 grams of PFBZPA and PEGPA were synthesized and purified. Large scale preparation of surface-modified $BaTiO_3$ (~20 g per batch) was performed and the FT-IR of each product confirmed that the surface modifications were successful at this scale. PFBZPA-modified $BaTiO_3$, both with and without BYK-W-9010, were each ball-milled for 1 day in DMF, followed by ball-milling with added Viton (50:50 volume). PEGPA-modified $BaTiO_3$, both with and without BYK-W-9010 were ball-milled for 1 day in pyridine followed by ball-milling with added PC (50:50 volume). The initial dispersions exhibited high viscosity and required subsequent ball-milling. These dispersions (or "sol") were used for thin film fabrication by spin coating on Al-coated glass slide.

g. KINETICS STUDY ON THE BINDING OF SURFACE MODIFIERS ON $BaTiO_3$ NANOPARTICLES

[00231] The kinetics of the binding of different anchoring groups appears to be very fast under usual surface modification conditions which have been used for modification (stirring at 80 °C in ethanol). The binding kinetics on untreated $BaTiO_3$ nanoparticles of four different head groups: trimethoxy silane, carboxylic acid, phosphonic acid, and sulfonic acid salt were investigated. While stirring at 80 °C, aliquots of the bulk reaction mixture were taken after 1 hour and 24 hours. The quenched reaction mixtures were washed immediately with a cold ethanol:water mixture by repeated centrifugation, followed by drying under vacuum at 80 °C. Normalized FT-IR absorption spectra showed little difference in all four head groups implying that the binding kinetics were fast and reached equilibrium within an hour (see Figure 19). The decrease in the peak height of ν_{CH} stretching modes from octyl chains in surface modifiers other than phosphonic acid depends on the washing conditions used. In this experiment, the washing conditions were more rigorous than that used previously.

4. CHARACTERIZATION – CAPACITANCE AND THICKNESS

[00232] The capacitance of the devices was measured in a humidity- and oxygen-controlled glove box on a probe station with 5 μm sharp tips. C_p at 1 kHz and 1 V_{RMS} was

measured from parallel equivalent LCR circuit on an Agilent 4284A LCR meter. The thickness of the films was measured for all the devices tested by measuring the film thickness from the base plane (bare aluminum) to the point as close as possible to the device edge by Tencor KLA P15 contact profilometer.

[00233] As the measured capacitances from different composite films are summarized in table 3 (summary of the capacitance measurements from different composites). BP: unmodified barium titanate in polycarbonate, PBP: PEGPA-barium titanate in polycarbonate, BV: unmodified barium titanate in Viton, FBV: PFBZPA-barium titanate in Viton, FBP: PFBZPA-barium titanate in polycarbonate, the suffix –B indicates the use of additional commercial dispersant, BYK-w-9010 (BYK Chemie)), the overall capacitance values were low, possibly due to the small dielectric constant of the barium titanate nanoparticles used. The dielectric constant of the nanoparticles calculated from theoretical models (Lichtenecker model and modified Kerner equation) yielded only about 150, which is significantly lower than that generally considered for barium titanate nanoparticles (at least 3,000). See also Figure 20.

Table 3

Composition	k (1kHz, 1V)	Average k	Composition	k (1kHz, 1V)	Average k
50BP-B	17.8	18.1+/- 0.4	50BV-B	11.9	14.0 +/- 2.9
	18.4			16.0	
50PBP	17.2	19.9 +/- 2.8	50FBV	38.3	36.9 +/- 1.4
	22.7			36.9	
	19.7			35.6	
50PBP-B	18.2	17.1 +/- 1.6	50FBV-B	31.2	33.4 +/- 2.2
	15.9			32.8	
50FBP	17.4	19.1 +/- 2.4		33.0	
	20.8			36.4	

[00234] Values from defective or poor quality films were excluded. Each value in table 3 represents an average of at least four independent measurements from the same film.

Films from phosphonic acid-modified barium titanate nanoparticles yielded higher dielectric constants than that of similar compositions containing unmodified nanoparticles, indicating that the resulting dielectric constant of the composite films is related to the level of dispersion. This may be further supported by comparing the leakage current densities and breakdown strengths of the composite films. The use of BYK-w-9010 dispersant enabled the formation of stable dispersions and fabrication of spin-coated films of acceptable quality. Phosphonic acid surface modifiers appear to provide slightly better dispersability and processability of the barium titanate-polymer sol than BYK-w-9010 at this volume fraction. When both the phosphonic acid modifier and BYK-w-9010 were used, the dielectric constant of the composite films decreased slightly. This may be explained by the increased volume fraction of organic phase in such dispersions.

5. LEAKAGE CURRENT DENSITY AND BREAKDOWN FIELD MEASUREMENTS

[00235] Leakage current density was measured for selected devices by applying a DC bias, up to 100 V_{DC}, across the device while monitoring the current with an Agilent E5272A source/monitor unit. Dielectric breakdown strength was subsequently measured using a Keithley 248 high voltage supply which provided a voltage sweep from 50 V_{DC} to the point of catastrophic device failure with an approximately 10 V/sec ramp rate. The average breakdown field from 4-6 different devices was taken as the reported dielectric breakdown voltage. For all characterization experiments, instrument control and data collection were automated using LabVIEW software.

[00236] Slightly higher leakage current in the films with BYK-w-9010 was expected than those without BYK-w-9010, since the polymeric surfactant can have unbound free acid groups which can be ionized and act as charge carriers. As shown in Figure 21, the leakage current at this volume fraction showed slight difference between the samples with and without BYK-w-9010. The overall leakage current was kept below 0.1 nA and 2 nA at 100 V_{DC} for polycarbonate-based capacitors and P(VDF-HFP)-based capacitors, respectively.

[00237] The capacitance and the loss tangent (dissipation factor) as a function of frequency are shown in Figure 22, where the two properties mainly depended on the host material's property and were not significantly affected by the surfactant. The overall frequency response showed little decrease in the capacitance and the loss tangent was kept

below 0.01 for polycarbonate-based devices and below 0.08 for P(VDF-HFP)-based devices.

[00238] The dielectric breakdown field was measured for selected representative devices and shown in Figure 23.

[00239] The breakdown field varied and average values were taken as reported values. Good working devices, fabricated from PBP and FBV nanocomposites, showed breakdown fields as large as 240 V/μm and 260 V/μm. From the average dielectric constant at 1 kHz, the capacitances of a hypothetical device of 1 cm^2 area and 1 μm thickness were calculated for each composite. The capacitance values were then used to calculate maximum energy stored in such a device by the following relation.

$$E = \frac{1}{2} CV^2$$

[00240] Figure 24 shows the maximum energy stored and maximum pulse power at 1 MHz calculated by taking the dissipation factor at this frequency and ignoring the slight decrease of dielectric constant of the materials at the frequency. These devices, although they have not been fully optimized, can store energy as high as 6 J/cc, which is greater than the "state-of-the-art" values of commercially available high energy density capacitors (2-5 J/cc).

6. Characterization and Surface Modification of New BT Nanoparticles

[00241] Barium titanate nanoparticles (BT150), obtained from TPL, Inc., were characterized by XRD, SEM, TEM, and FT-IR. As shown in Figure 25, the crystalline structure of BT150 has more tetragonality than Aldrich BTs.

[00242] The size of BT150 is about 150 nm as observed by SEM (figure 26) and TEM, which is close to the manufacturer's spec. (142 nm). The BET surface area provided by the manufacturer was 7.22 m^2/g. This value was used to calculate stoichiometric amount of surface modifiers for surface modification reactions.

7. SEM OF THE CAPACITORS PREPARED FROM ALDRICH BT COMPOSITES

[00243] Small cut and cross-sectioned devices were prepared for analysis by fracturing the devices immediately after cooling in LN2 followed by gold conductive coating. A LEO 1530 TFE-SEM with In-Lens detector was used. The images were acquired at 20kV acceleration voltage at 1-2 mm WD (working distance).

8. COMPARISON OF SURFACE HYDROXYL DENSITIES AND SURFACE PRETREATMENT TO INCREASE SURFACE HYDROXYL CONCENTRATION

[00244] BT's from different sources (Aldrich, Inframat Advanced Materials Co., TPL Inc., and Cabot Corp.) were rigorously dried in a vacuum oven at 90 °C for 1 day, followed by FT-IR analysis. Attempts were made to increase surface hydroxyl on BT150 using oxygen plasma treatment and acid/base treatment. Oxygen plasma treatment was performed with both "as-received" and "pre-dried" BT150 powders (TPL, Inc.) for 1, 5, and 10 minutes. Acid/base pre-treatment on *ca.* 0.5 g BT150 was done in approximately 10 mL of aqueous HCl (pH = 1.05) and NaOH (pH = 12.81) for 48 hours. The treated particles were thrice washed by centrifuge with 15 mL of distilled deionized water, followed by drying under vacuum. The molecular weight of the polycarbonate resins (PolySciences) was determined by gel permeation chromatography to be Mn = 23,700, Mw = 47,400 (PDI = 1.99).

9. SEM CHARACTERIZATION OF DEVICES FABRICATED FROM ALDRICH BT NANOPARTICLES

[00245] The PEGPA-modified $BaTiO_3$ nanoparticles resulted in uniform films in polycarbonate host with no observable defects in both with and without BYK-w-9010 surfactant, while the films made from uncoated nanoparticles developed cracks on the surface as well as pinholes resulting from these cracks as observed in cross-sectional images (see Figure 27). These cracks are generally caused by mechanical stress during the drying procedure and are more likely to develop under non-uniform drying conditions.

[00246] Figure 28 shows SEM images of Viton-based films with pronounced contrast between the films of unmodified BT and modified BT. The surface morphology was not as uniform as PC-based films but the best quality was from PFBZPA-BT without BYK-w-

9010 implying that BYK-w-9010 is not very compatible with Viton. This is supported by the poor quality of unmodified BT:Viton with BYK-w-9010 film. It should be noted that the dielectric constant of unmodified BT:Viton (14.0) was even less than that of unmodified BT:PC (18.1).

10. EXAMPLE 15

[00247] BT150 was purchased and the same series of experiments were performed as was done with the Aldrich BTs. Figure 29 shows the FT-IR spectra of as-received and NH_4Cl-washed BT150. $BaCO_3$ impurity could be successfully removed by the same methodology used for Aldrich BTs.

[00248] The relative intensity of O-H stretching mode in FT-IR spectra of dried BT nanoparticles was significantly varying for different nanoparticles probably due to the differences in the production methods (Figure 30). The density of surface hydroxyl group on BT surface turned out to be a factor in successful surface modification with phosphonic acids. While not wishing to be bound by any particular theory, many literature sources report the binding mechanisms of phosphonic acid and phosphonate esters on titania, alumina, and zirconia surfaces is the condensation between two hydroxyl groups, i.e., P-OH and M-OH. Other mechanisms, such as the coordination of phosphoryl oxygen to electron deficient Lewis acid sites followed by base catalyzed hydrolysis can exist, but the condensation mechanism is believed dominant. Without wishing to be bound by theory, it is believed that the higher the density of surface hydroxyl, the larger the coverage by phosphonic acid on BT.

[00249] Since the BT150 has relatively low amount of surface hydroxyl group, it resulted in poor surface modifications by both PEGPA and PFBZPA (Figure 31).

[00250] Dispersions with these poorly-coated nanoparticles were not very stable and formed films with large aggregates and defects. Consequently, the measured dielectric constants were smaller than those of the films prepared by using BYK-w-9010 as shown in Figure 32. However, it was observed that the BT150 had higher permittivity than Aldrich BTs (~150). Therefore, BT nanoparticles with sufficient permittivity (> 1,000) bearing as much surface hydroxyl groups as possible are the most desirable material.

[00251] To increase the surface hydroxyl groups on BT150, oxygen plasma treatment and acid/base treatment were performed. While the oxygen plasma gave little effect on the surface hydroxyl, both acid and base treatment resulted in the increase of surface hydroxyl groups. The size and shape of BT150 nanoparticles after acid/base treatment showed no noticeable changes under SEM. BT8 is a desirable nanoparticle for modification due to its high surface hydroxyl group concentration and high permittivity.

[00252] It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

CLAIMS

What is claimed is:

1. A coated metal oxide nanoparticle comprising:

    a. a ternary or higher order metal oxide nanoparticle having a surface; and

    b. phosphonic acid ligands attached to the metal oxide nanoparticle surface.

2. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticles range in size between about 20 and about 500 nanometers.

3. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticles range in size between about 49 and about 120 nanometers.

4. The coated metal oxide nanoparticle of claim 1, wherein the coated metal oxide nanoparticles range in size between about 60 and about 100 nanometers.

5. The coated metal oxide nanoparticle of claim 1, wherein the coated metal oxide nanoparticles range in size between about 20 and about 40 nanometers.

6. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide has a ferroelectric phase in the bulk.

7. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle has a ferroelectric phase.

8. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle comprises one or more perovskites, distorted perovskites, or a mixture thereof.

9. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle comprises a distorted perovskite.

10. The coated metal oxide nanoparticle of claim 8, wherein at least one of the perovskites has the formula ABO_3, wherein A and B are metal cations of different sizes.

11. The coated metal oxide nanoparticle of claim 8, wherein at least one of the perovskites has the formula $ATiO_3$, wherein A is a metal cation selected from Ba and Sr.

12. The coated metal oxide nanoparticle of claim 8, wherein at least one of the perovskites is a distorted perovskite having the formula $A_{(1-x)}B_{(1+x)}O_3$, wherein A and B are metal cations of different sizes and x is a number less than 1 and greater than zero 0.

13. The coated metal oxide nanoparticle of claims 10-12, wherein A and B are selected from the group consisting of titanium, manganese, copper, tungsten, niobium, bismuth, zirconium, lead, lithium, strontium, lanthanum, and ruthenium.

14. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle comprises $Pb(Zr,Ti)O_3$, and $(Ba,Sr)TiO_3$.

15. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide comprises a composition of about $BaTi_{0.8}Zr_{0.2}O_3$.

16. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle comprises $Pb(Zr,Ti)O_3$.

17. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle selected from the group consisting of a titanate-based ferroelectric; a manganate-based material; a cuprate-based material; a tungsten bronze-type niobate, tantalate or titanate or a layer bismuth tantalate, niobate, or titanate; bismuth titanate; strontium bismuth tantalate; strontium bismuth niobate; strontium bismuth tantalate niobate; lead zirconate titanate; lead lanthanum zirconate titanate; lead titanate; bismuth titanate; lithium niobate; lithium tantalate; strontium rhuthenate; barium titanate; and strontium titanate and mixtures thereof.

18. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle selected from the group consisting of $BaTiO_3$, $PbTiO_3$, and $SrTiO_3$.

19. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide selected from the group consisting of $BaTiO_3$, $SrTiO_3$, and $BaTi_{0.8}Zr_{0.2}O_3$.

20. The coated metal oxide nanoparticle of claim 1, wherein the metal oxide nanoparticle comprises $BaTiO_3$.

21. The coated metal oxide nanoparticle of claim 1, wherein TiO_2 and Al_2O_3 are substantially absent.

22. The coated metal oxide nanoparticle of claim 1, wherein the at least one organic phosphonic acid comprises *n*-octylphosphonic acid, methylphosphonic acid, 11-hydroxyundecylphosphonic acid, octadecylphosphonic acid, (11-phosphonoundecyl)phosphonic acid, (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phosphonic acid, benzylphosphonic acid, {2-[2-(2-methoxyethoxy)ethoxy]ethyl}phosphonic acid, [3-(4-{[4'-(phenyl-*m*-tolylamino)biphenyl-4-yl]-*m*-tolylamino}phenoxy)propyl]-phosphonic acid, (11-prop-2-ynyloxyundecyl)phosphonic acid, pentafluorobenzylphosphonic acid, pentabromobenzylphosphonic acid, (11-acryloyloxyundecyl)phosphonic acid, (11-cinnamoyloxyundecyl)phosphonic acid, 3-(9*H*-carbazol-9-yl)propylphosphonic acid, 3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)propylphosphonic acid, or pentabromobenzylphosphonic acid or a mixture thereof.

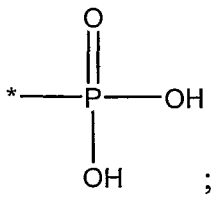
23. The coated metal oxide nanoparticle of claim 1, wherein the at least one phosphonic acid ligand comprises a residue of a compound having the structure:

$$G_n\text{-}R\text{-}X_n,$$

wherein G is a terminal group;

wherein R is a bridging group;

wherein X is a phosphonic acid group having the structure:



; and

wherein each n is, independently, 1, 2, or 3.

24. The coated metal oxide nanoparticle of claim 23, wherein each n is 1.

25. The coated metal oxide nanoparticle of claim 23, wherein the compound comprises the structure G-R-X.

26. The coated metal oxide nanoparticle of claim 25, wherein the terminal group comprises an alkyl, a perfluoroalkyl, an aryl, a perfluroaryl, a hydroxyl, an amine, an amide, an ester, a thiol, a selenol, a phosphine, a phosphonic acid, or a phosphonate ester group.

27. The coated metal oxide nanoparticle of claim 25, wherein the terminal group is a luminescent group comprising an organic dye.

28. The compound of claim 25, wherein the terminal group is a polarizable group comprising a *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine or a C_{60}.

29. The compound of claim 25, wherein the terminal group is a polymerizable group comprising a vinyl, an allyl, a styryl, an acroyl, an epoxide, an oxetane, a cyclic-carbonate, a methacroyl, an acrylonitrile, an isocyanate, an isothiocyanate, or a strained ring olefin group.

30. The coated metal oxide nanoparticle of claim 25, wherein the terminal group is a polymerizable group comprising a strained ring olefin group selected from dicyclopentadienyl, norbornyl, and cyclobutenyl.

31. The coated metal oxide nanoparticle of claim 25, wherein the terminal group is a polymerizable group comprising $-(CH_2)\eta SiCl_3$, $-(CH_2)\eta Si(OCH_2CH_3)_3$, or $-(CH_2)\eta Si(OCH_3)^3$, wherein η is an integer from 0 to 25.

32. The coated metal oxide nanoparticle of claim 25, wherein the terminal group is a cross-linkable group comprising chalcone, cinnamate, vinyl, cyclooact-4-eneyl, alkyne, azide, succinamide, or maleimide.

33. The coated metal oxide nanoparticle of claim 25, wherein the terminal group is a coordinating group comprising a crown ether or ethylenediaminetetraacetic acid.

34. The coated metal oxide nanoparticle of claim 25, wherein R comprises a substituted or unsubstituted, linear or branched, C_3 to C_{50} aliphatic or cyclic aliphatic, fluoroalkyl, oligo(ethyleneglycol), aryl, or amino group.

35. The coated metal oxide nanoparticle of claim 25, wherein G is an amino group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta NR_{a2}R_{a3}$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha NR_{a2}R_{a3}$, $-(CF_2)_\beta CH_2NR_{a2}R_{a3}$, $-OCHCH_2-(CF_2)_\beta CH_2NR_{a2}R_{a3}$, or $-O(CF_2)_\beta CH_2NR_{a2}R_{a3}$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, and wherein R_{a2} and R_{a3} independently comprise H, a linear or branched alkyl group having up to 25 carbons.

36. The coated metal oxide nanoparticle of claim 25, wherein G is a halogen and R and G together comprise $-(CH_2CH_2O)_\gamma-(CH_2)_\delta F$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Cl$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Br$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta I$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha F$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha Cl$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha Br$, or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha I$, wherein γ is an integer from 0 to 25, wherein δ is an integer from 0 to 25, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25.

37. The coated metal oxide nanoparticle of claim 25, wherein G is a cyano group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CN$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha CN$, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25.

38. The coated metal oxide nanoparticle of claim 25, wherein G is a aldehyde group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CHO$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha CHO$, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25.

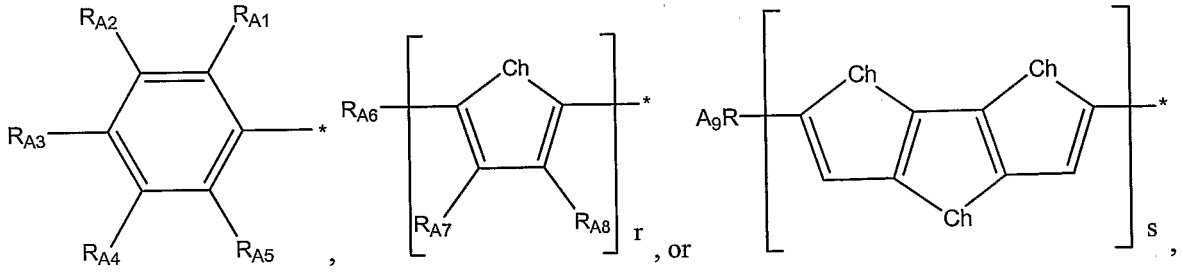
39. The coated metal oxide nanoparticle of claim 25, wherein G is a nitro group and R and G together comprise $-(CH_2CH_2O)_\gamma-(CH_2)_\delta NO_2$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha NO_2$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein γ is an integer from 0 to 25, and wherein δ is an integer from 0 to 25.

40. The coated metal oxide nanoparticle of claim 25, wherein G is an alkyl group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta OR_{a1}$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta$-CCH, $-(CH_2)_\beta-$

$(CH_2CH_2O)_\alpha$-CCH, -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$-$CHCH_2$, -$(CH_2)_\beta$-$(CH_2CH_2O)_\alpha$-$CHCH_2$, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$-R_{a1}, -$(CF_2)_\beta OR_{a1}$, -$(CF_2)_\beta CF_3$, -$O(CF_2)_\beta OR_{a1}$, or -$OCHCH_2$-$(CF_2)_\beta$-OR_{a1}, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, and wherein R_{a1} comprises H, a linear or branched alkyl group having up to 25 carbons.

41. The coated metal oxide nanoparticle of claim 25, wherein G is a fluorinated group and R and G together comprise -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha F$, -$OCHCH_2$-$(CF_2)_\beta CF_3$, -$(CF_2CF_2)_\alpha$-$(CF_2)_\beta CF_3$, -$(CF_2)_\beta$-$(CF_2CF_2)_\alpha CF_3$, -$(CF_2CF_2)_\alpha$-$(CH_2)_\beta CF_3$, or -$(CF_2)_\beta$-$(CF_2CF_2)_\alpha CF_3$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25.

42. The coated metal oxide nanoparticle of claim 25, wherein G is an aromatic group and R and G together comprise -$(CH_2CH_2O)_\alpha$-$(CH_2)_\beta$-Phenyl, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Phenyl, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Phenyl, -$(CF_2)_\beta$-$(OCH_2CH_2)_\alpha$Phenyl, -$(CH_2)_\beta$-$(OCH_2CH_2)_\alpha$Aryl, -$(CF_2)_\beta$-$(OCH_2CH_2)_\alpha$Aryl, -$(OCH_2CH_2)_\alpha$-$(CF_2)_\beta$Aryl, -$(OCH_2CH_2)_\alpha$-$(CH_2)_\beta$Aryl, -$O(CH_2)_\beta$Aryl, or -O-$(CF_2)_\beta$Aryl, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein Aryl is



wherein Ch is Se, S, or O, wherein r is an integer from 0 to 50, wherein s is an integer from 0 to 3, and wherein R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, R_{A6}, R_{A7}, R_{A8}, and R_{A9} independently comprise -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta OCH_3$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta N(CH_3)_3$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta CON(CH_3)_2$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta CN$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta F$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta NO_2$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta CHO$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta Cl$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta Br$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta I$, -$(CH_2CH_2O)_\gamma$-$(CH_2)_\delta$Phenyl, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma CH_3$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\delta N(CH_3)_2$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma CON(CH_3)_2$, -$(CH_2)_\delta$-$(CH_2CH_2O)_\gamma CN$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma F$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma NO_2$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma CHO$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma Cl$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma Br$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma I$, -$(CH_2)_\delta$-$(OCH_2CH_2)_\gamma$Phenyl, -$(CF_2)_\beta OCH_3$, -$(CF_2)_\beta CH_2ON(CH_3)_2$, -

$(CF_2)_\beta CF_3$, $-O(CF_2)_\beta OCH$, $-OCH_2CH_2-(CF_2)_\beta OCH$, $-OCH_2CH_2-(CF_2)_\beta CH_2N(CH_3)_2$, $-O(CF_2)_\beta CH_2N(CH_3)_2$, $OCH_2CH_2-(CF_2)_\beta CHO$, $-O(CF_2)_\beta CHO$, $-OCH_2CH_2-(CF_2)_\beta CF_3$, $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, or $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, wherein γ is an integer from 0 to 25, and wherein δ is an integer from 0 to 25.

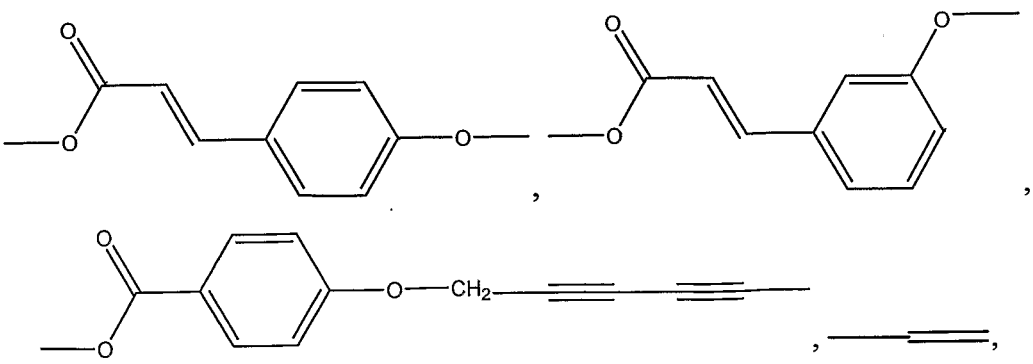
43. The coated metal oxide nanoparticle of claim 25, wherein G is an ionic group comprising SO_3^-, $-NR^{11}{}_3^+$, $-PO_3H^-$, $-PO_3^{2-}$, or $-COO^-$, wherein each R^{11} is independently selected from H or alkyl.

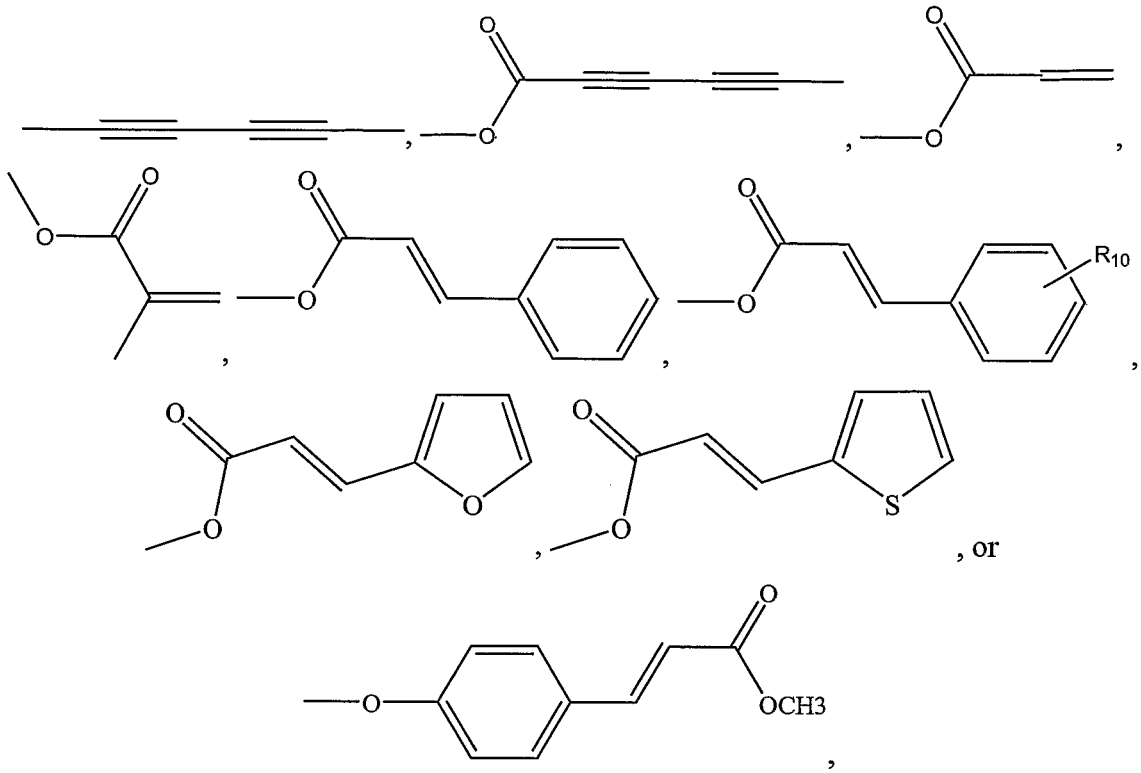
44. The coated metal oxide nanoparticle of claim 25, wherein G is a polymerizable group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-CH=CH_2$ or $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-CH=CH_2$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25.

45. The coated metal oxide nanoparticle of claim 25, wherein G is a cross-linkable group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-C\equiv CH$, $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-C\equiv CH$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-N_3$, or $-(CH2)_\beta-(CH_2CH_2O)_\alpha-N_3$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25.

46. The coated metal oxide nanoparticle of claim 25, wherein G is an amide group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CONR_{a2}R_{a3}$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha CONR_{a2}R_{a3}$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein R_{a2} and R_{a3} independently comprise H, a linear or branched alkyl group having up to 25 carbons.

47. The coated metal oxide nanoparticle of claim 25, wherein the polymerizable group comprises a residue of:

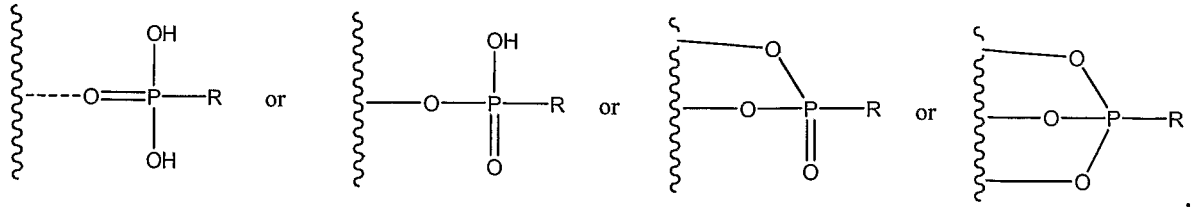




wherein R_{10} is a linear or branched alkyl group having up to 25 carbons.

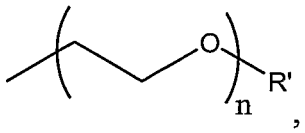
48. The coated metal oxide nanoparticle of claim 1, wherein the phosphonic acid ligands are attached to the surface by bonds ranging from covalent, to polar covalent, to ionic, and including through hydrogen bonding, of one, two, or three of the oxygen atoms of the phosphonic acid ligands to the metal oxide surface.

49. The coated metal oxide nanoparticle of claim 1, wherein the organic phosphonic acid ligands are attached to the surface by bonding as illustrated by one or more of the structures illustrated below:



50. The coated metal oxide nanoparticle of claim 49, wherein R is an organic radical comprising 1 to 18 carbon atoms.

51. The coated metal oxide nanoparticle of claim 49, wherein R is an alkyl substituted polyether having the structure



wherein n is 1 to 25, and R' is a C1-C4 alkyl.

52. The coated metal oxide nanoparticle of claim 49, wherein R is selected from methyl, ethyl propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl.

53. The coated metal oxide nanoparticle of claim 49, wherein R is a residue of a polymer.

54. The coated metal oxide nanoparticle of claim 49, wherein R is a residue of an epoxy, a polyimide, a cyanate ester or polyurethane, a polyvinylidene difluoride, a fluoropolymer, a polyester, a polycarbonate, a polycarbonate-carbonate, a polyether-ketone, a polyphenylene oxide, or a polyphenylene sulfide, a polyvinylphenol, a polyvinylpyrrolidinone, a polyolefin, polyester, polyethylene naphthalate, cyanoethylated pullulan and other pulluan esters, siloxane polymers, and copolymers of a vinylidenefluoride or a trifluoroethylene or a chlorotrifluoroethylene or a hexafluoropropylene or a copolymers thereof.

55. The coated metal oxide nanoparticle of claim 49, wherein R is a residue of epoxy resin, a polyimide resin, a cyanate ester, a polyvinylidene difluoride, a fluoropolymer, a polyester, a polycarbonate, a polycarbonate-carbonate, a polyether-ketone, a polyphenylene oxide, or a polyphenylene sulfide, or copolymers thereof.

56. The coated metal oxide nanoparticle of claim 49, wherein X, R, and G together comprise *n*-octylphosphonic acid, methylphosphonic acid, 11-hydroxyundecylphosphonic acid, octadecylphosphonic acid, (11-phosphonoundecyl)phosphonic acid, (3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phosphonic acid, benzylphosphonic acid, {2-[2-(2-methoxyethoxy)ethoxy]ethyl}phosphonic acid, [3-(4-{[4′-(phenyl-*m*-tolylamino)biphenyl-4-yl]-*m*-tolylamino}phenoxy)propyl]-phosphonic acid, (11-prop-2-ynyloxyundecyl)phosphonic acid, pentafluorobenzylphosphonic acid,

pentabromobenzylphosphonic acid, (11-acryloyloxyundecyl)phosphonic acid, (11-cinnamoyloxyundecyl)phosphonic acid, 3-(9*H*-carbazol-9-yl)propylphosphonic acid, 3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)propylphosphonic acid, or pentabromobenzylphosphonic acid.

57. The coated metal oxide nanoparticle of claim 1, wherein the phosphonic acid ligands form a coating on the surface of the metal oxide nanoparticle.

58. The coated metal oxide nanoparticle of claim 1, wherein the phosphonic acid ligands sufficiently cover the metal oxide nanoparticle surface to form an approximately full monolayer on the metal oxide nanoparticle surface.

59. The coated metal oxide nanoparticle of any of claims 1 to 58, wherein the organic phosphonic acid ligands are present in a concentration of at least about 5 ligands per nm^2 of metal oxide surface area.

60. The coated metal oxide nanoparticle of any of claims 1 to 58, wherein the phosphonic acid ligands are present in a concentration of from about 8 ligands per nm^2 to about 10 ligands per nm^2 of metal oxide surface area.

61. A coated metal oxide nanoparticle comprising:

    a. a metal oxide nanoparticle having a surface; and

    b. ligands selected from residues of phosphonic acids, thiophosphonic acids, dithiophosphonic acids, trithiophosphonic acids, phosphinic acids, thiophosphinic acids, dithiophosphinic acids, phosphohydroxamic acids, and thiophosphohydroxamic acids and derivatives thereof and mixtures thereof attached to the metal oxide nanoparticle surface.

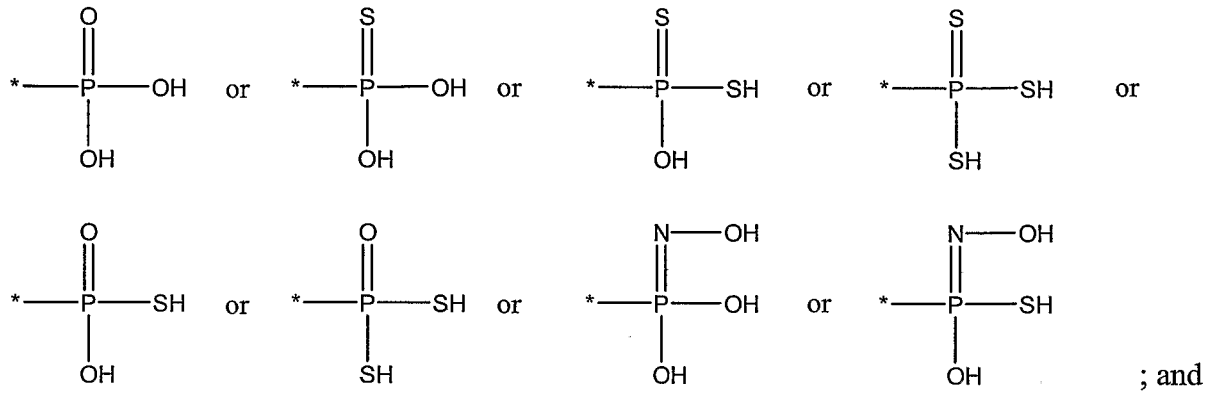
62. The coated metal oxide nanoparticle of claim 61, wherein the ligands comprise residues of compounds having the structure:

$$G_n\text{-}R\text{-}X_n,$$

wherein G is a terminal group;

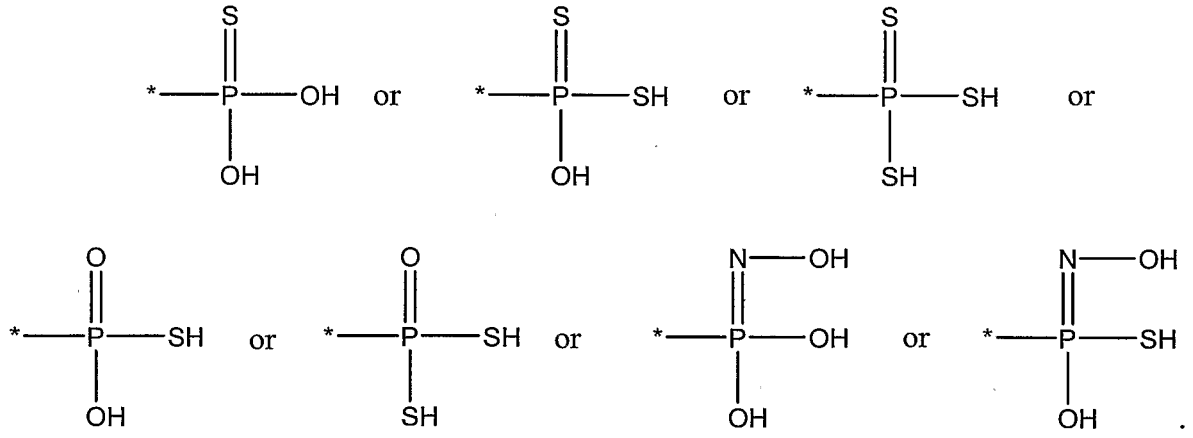
wherein R is a bridging group;

wherein X is selected from:



wherein each n is, independently, 1, 2, or 3.

63. The coated metal oxide nanoparticle of claim 23, wherein X is selected from:



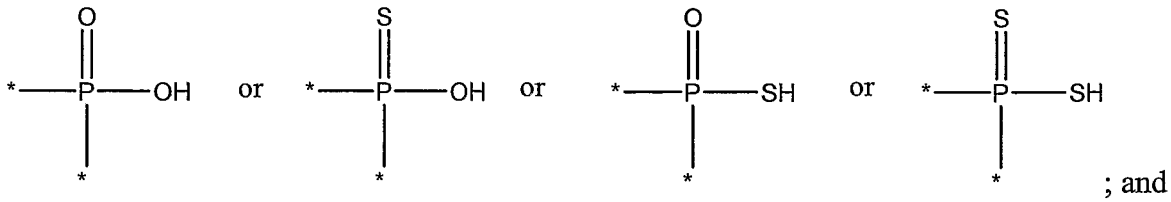
64. The coated metal oxide nanoparticle of claim 61, wherein the ligands comprise residues of compounds having the structure:

$$G_n\text{-}R\text{-}X_n,$$

wherein G is a terminal group;

wherein R is a bridging group;

wherein X is selected from:



; and

wherein each n is, independently, 1, 2, or 3.

65. The coated metal oxide nanoparticle of claim 23, wherein each n is 1.

66. The coated metal oxide nanoparticle of claim 23, wherein the compound comprises the structure G-R-X.

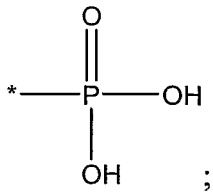
67. A phosphonic acid compound comprising the structure:

$$G_n\text{-}R\text{-}X_n,$$

wherein G is a terminal group;

wherein R is a bridging group;

wherein X is a phosphonic acid group having the structure:



; and

wherein each n is, independently, 1, 2, or 3.

68. The compound of claim 60, wherein each n is 1.

69. The compound of claim 60, wherein the compound comprising the structure G-R-X.

70. The compound of claim 60, wherein the at least one organic phosphonic acid is present as *n*-octylphosphonic acid, methylphosphonic acid, 11-hydroxyundecylphosphonic acid, octadecylphosphonic acid, (11-phosphonoundecyl)phosphonic acid,

(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)phosphonic acid, benzylphosphonic acid, {2-[2-(2-methoxyethoxy)ethoxy]ethyl}phosphonic acid, [3-(4-{[4′-(phenyl-*m*-tolylamino)biphenyl-4-yl]-*m*-tolylamino}phenoxy)propyl]-phosphonic acid, (11-prop-2-ynyloxyundecyl)phosphonic acid, pentafluorobenzylphosphonic acid, pentabromobenzylphosphonic acid, (11-acryloyloxyundecyl)phosphonic acid, (11-cinnamoyloxyundecyl)phosphonic acid, 3-(9*H*-carbazol-9-yl)propylphosphonic acid, 3-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)propylphosphonic acid, or pentabromobenzylphosphonic acid or a mixture thereof.

71. The compound of claim 69, wherein the terminal group comprises an alkyl, a perfluoroalkyl, an aryl, a perfluroaryl, a hydroxyl, an amine, an amide, an ester, a thiol, a selenol, a phosphine, a phosphonic acid, or a phosphonate ester group.

72. The compound of claim 69, wherein the terminal group is a luminescent group comprising an organic dye.

73. The compound of claim 69, wherein the terminal group is a polarizable group comprising a *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine or a C_{60}.

74. The compound of claim 69, wherein the terminal group is a polymerizable group comprising a vinyl, an allyl, a styryl, an acroyl, an epoxide, an oxetane, a cyclic-carbonate, a methacroyl, an acrylonitrile, an isocyanate, an isothiocyanate, or a strained ring olefin group.

75. The compound of claim 69, wherein the terminal group is a polymerizable group comprising a strained ring olefin group selected from dicyclopentadienyl, norbornyl, and cyclobutenyl.

76. The compound of claim 69, wherein the terminal group is a polymerizable group comprising $-(CH_2)\eta SiCl_3$, $-(CH_2)\eta Si(OCH_2CH_3)_3$, or $-(CH_2)\eta Si(OCH_3)_3$, wherein η is an integer from 0 to 25.

77. The compound of claim 69, wherein the terminal group is a cross-linkable group comprising chalcone, cinnamate, vinyl, cyclooact-4-eneyl, alkyne, azide, succinamide, or maleimide.

78. The compound of claim 69, wherein the terminal group is a coordinating group comprising a crown ether or ethylenediaminetetraacetic acid.

79. The compound of claim 69, wherein R comprises a substituted or unsubstituted, linear or branched, C_3 to C_{50} aliphatic or cyclic aliphatic, fluoroalkyl, oligo(ethyleneglycol), aryl, or amino group.

80. The compound of claim 69, wherein G is an amino group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta NR_{a2}R_{a3}$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha NR_{a2}R_{a3}$, $-(CF_2)_\beta CH_2NR_{a2}R_{a3}$, $-OCHCH_2-(CF_2)_\beta CH_2NR_{a2}R_{a3}$, or $-O(CF_2)_\beta CH_2NR_{a2}R_{a3}$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, and wherein R_{a2} and R_{a3} independently comprise H, a linear or branched alkyl group having up to 25 carbons.

81. The compound of claim 69, wherein G is a halogen and R and G together comprise $-(CH_2CH_2O)_\gamma-(CH_2)_\delta F$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Cl$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta Br$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta I$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha F$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha Cl$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha Br$, or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha I$, wherein γ is an integer from 0 to 25, wherein δ is an integer from 0 to 25, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25.

82. The compound of claim 69, wherein G is a cyano group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CN$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha CN$, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25.

83. The compound of claim 69, wherein G is a aldehyde group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CHO$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha CHO$, wherein α is an integer from 0 to 25, and wherein β is an integer from 0 to 25.

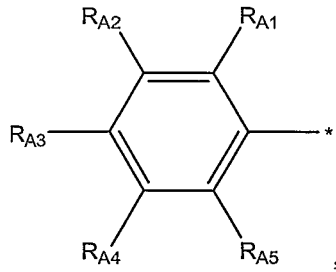
84. The compound of claim 69, wherein G is a nitro group and R and G together comprise $-(CH_2CH_2O)_\gamma-(CH_2)_\delta NO_2$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha NO_2$, wherein α is an integer from 0 to

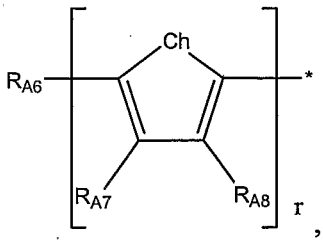
25, wherein β is an integer from 0 to 25, wherein γ is an integer from 0 to 25, and wherein δ is an integer from 0 to 25.

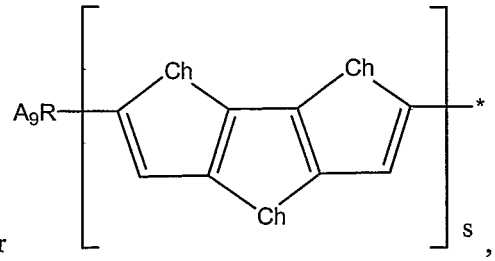
85. The compound of claim 69, wherein G is an alkyl group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta OR_{a1}$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-CCH$, $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-CCH$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-CHCH_2$, $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-CHCH_2$, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha-R_{a1}$, $-(CF_2)_\beta OR_{a1}$, $-(CF_2)_\beta CF_3$, $-O(CF_2)_\beta OR_{a1}$, or $-OCHCH_2-(CF_2)_\beta-OR_{a1}$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, and wherein R_{a1} comprises H, a linear or branched alkyl group having up to 25 carbons.

86. The compound of claim 69, wherein G is a fluorinated group and R and G together comprise $-(CH_2)_\beta-(OCH_2CH_2)_\alpha F$, $-OCHCH_2-(CF_2)_\beta CF_3$, $-(CF_2CF_2)_\alpha-(CF_2)_\beta CF_3$, $-(CF_2)_\beta-(CF_2CF_2)_\alpha CF_3$, $-(CF_2CF_2)_\alpha-(CH_2)_\beta CF_3$, or $-(CF_2)_\beta-(CF_2CF_2)_\alpha CF_3$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25.

87. The compound of claim 69, wherein G is an aromatic group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta$-Phenyl, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, $-(CH_2)_\beta-(OCH_2CH_2)_\alpha$Aryl, $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Aryl, $-(OCH_2CH_2)_\alpha-(CF_2)_\beta$Aryl, $-(OCH_2CH_2)_\alpha-(CH_2)_\beta$Aryl, $-O(CH_2)_\beta$Aryl, or $-O-(CF_2)_\beta$Aryl, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein Aryl is



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wherein Ch is Se, S, or O, wherein r is an integer from 0 to 50, wherein s is an integer from 0 to 3, and wherein R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, R_{A6}, R_{A7}, R_{A8}, and R_{A9} independently comprise $-(CH_2CH_2O)_\gamma-(CH_2)_\delta OCH_3$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta N(CH_3)_3$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta CON(CH_3)_2$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta CN$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta F$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta NO_2$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta CHO$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta Cl$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta Br$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta I$, $-(CH_2CH_2O)_\gamma-(CH_2)_\delta$Phenyl, $-(CH_2)_\delta-$

$(OCH_2CH_2)_\gamma CH_3$, $-(CH_2)_\delta-(OCH_2CH_2)_\delta N(CH_3)_2$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma CON(CH_3)_2$, $-(CH_2)_\delta-(CH_2CH_2O)_\gamma CN$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma F$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma NO_2$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma CHO$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma Cl$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma Br$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma I$, $-(CH_2)_\delta-(OCH_2CH_2)_\gamma$Phenyl, $-(CF_2)_\beta OCH_3$, $-(CF_2)_\beta CH_2ON(CH_3)_2$, $-(CF_2)_\beta CF_3$, $-O(CF_2)_\beta OCH$, $-OCH_2CH_2-(CF_2)_\beta OCH$, $-OCH_2CH_2-(CF_2)_\beta CH_2N(CH_3)_2$, $-O(CF_2)_\beta CH_2N(CH_3)_2$, $OCH_2CH_2-(CF_2)_\beta CHO$, $-O(CF_2)_\beta CHO$, $-OCH_2CH_2-(CF_2)_\beta CF_3$, $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, or $-(CF_2)_\beta-(OCH_2CH_2)_\alpha$Phenyl, wherein γ is an integer from 0 to 25, and wherein δ is an integer from 0 to 25.

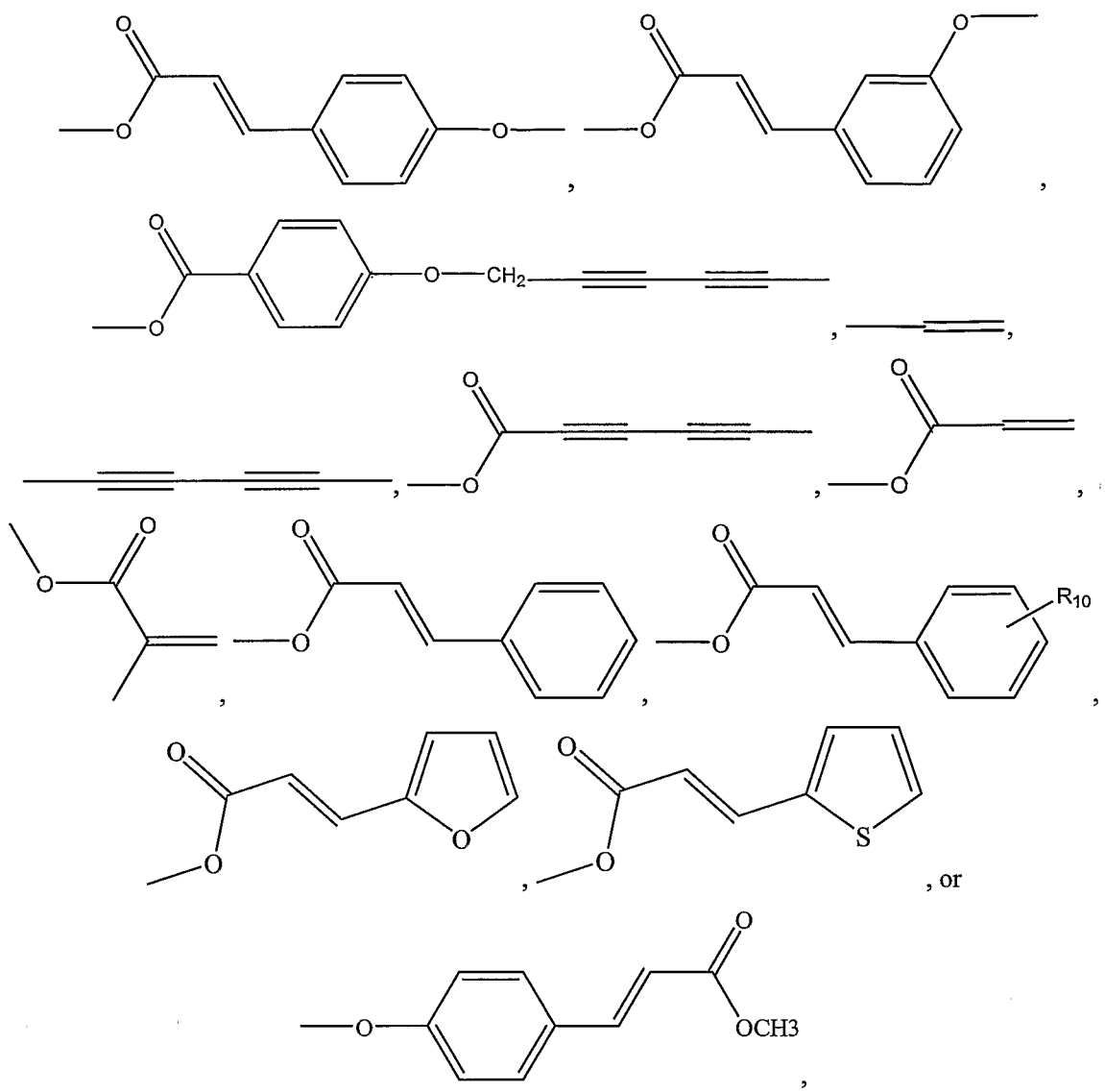
88. The compound of claim 69, wherein G is an ionic group comprising SO_3^-, $-NR^{11}{}_3^+$, $-PO_3H^-$, $-PO_3^{2-}$, or $-COO^-$, wherein each R^{11} is independently selected from H or alkyl.

89. The compound of claim 69, wherein G is a polymerizable group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-CH=CH_2$ or $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-CH=CH_2$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25.

90. The compound of claim 69, wherein G is a cross-linkable group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-C\equiv CH$, $-(CH_2)_\beta-(CH_2CH_2O)_\alpha-C\equiv CH$, $-(CH_2CH_2O)_\alpha-(CH_2)_\beta-N_3$, or $-(CH2)_\beta-(CH_2CH_2O)_\alpha-N_3$, wherein α is an integer from 0 to 25 and wherein β is an integer from 0 to 25.

91. The compound of claim 69, wherein G is an amide group and R and G together comprise $-(CH_2CH_2O)_\alpha-(CH_2)_\beta CONR_{a2}R_{a3}$ or $-(CH_2)_\beta-(OCH_2CH_2)_\alpha CONR_{a2}R_{a3}$, wherein α is an integer from 0 to 25, wherein β is an integer from 0 to 25, wherein R_{a2} and R_{a3} independently comprise H, a linear or branched alkyl group having up to 25 carbons.

92. The compound of claim 69, wherein the polymerizable group comprises a residue of


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94. The method of claim 93 further comprising a step of isolating and purifying the coated metal oxide nanoparticles.

95. The method of claim 93 wherein the step of providing the metal oxide nanoparticles comprises a step of treating or etching the surface of the metal oxide nanoparticles to at least partially remove any surface contaminants thereon.

96. A method for preparing the coated metal oxide nanoparticle of any of claims 1 to 60 comprising the steps of:

a. treating the metal oxide nanoparticle with an etchant; and

b. reacting the etched metal oxide nanoparticle with a compound of any of claims 67 to 92, wherein X is an anchoring group that can bind to the metal oxide nanoparticle.

97. The method of claim 96, wherein the etchant comprises aqueous NH_4Cl, aqueous HCl, or aqueous HNO_3.

98. The method of claim 96, further comprising the steps of purification and isolation of the coated metal oxide nanoparticle.

99. A nanocomposite composition comprising:

a. a polymer; and

b. the coated metal oxide nanoparticle of any of claims 1 to 60 dispersed within the polymer.

100. The nanocomposite composition of claim 99, wherein the polymer has a dielectric constant greater than or equal to 2.25 and less than 30 when measured at 1 kHz.

101. The nanocomposite composition of claim 99, wherein the polymer is soluble in an organic solvent.

102. The nanocomposite composition of claim 101, wherein the organic solvent is selected from the group consisting of tetrahydrofuran, acetonitrile, acetone, dimethylformamide, methanol, ethanol, and ethylene glycol.

103. The nanocomposite composition of claim 99, wherein the polymer is an epoxy, a polyimide, a cyanate ester or polyurethane, a polyvinylidene difluoride, a fluoropolymer such as Teflon or Viton, a polyester, a polycarbonate, a polycarbonate-carbonate, a polyether-ketone, a polyphenylene oxide, or a polyphenylene sulfide, a polyvinylphenol, polyvinylpyrrolidinone, polyolefin, polyester, polyethylene naphthalate, cyanoethylated pullulan and other pulluan esters, siloxane polymers, and copolymers of a vinylidenefluoride or a trifluoroethylene or a chlorotrifluoroethylene or a hexafluoropropylene or copolymers thereof or mixtures thereof.

104. The nanocomposite composition of claim 99, wherein the polymer is a polymer resin.

105. The nanocomposite composition of claim 99, wherein the polymer soluble in water.

106. A capacitor comprising at least one coated metal oxide nanoparticle of any of claims 1 to 60.

107. A capacitor comprising the nanocomposite composition of any of claims 99 to 106.

108. A method for preparing a coated nanoparticle comprising the steps of:

a. treating a metal oxide nanoparticle with an etchant; and

b. reacting the etched metal oxide nanoparticle with a compound of claim 69, wherein X is an anchoring group that can bind to the metal oxide nanoparticle

109. A method for preparing a film comprising the steps of:

a. dispersing the coated metal oxide nanoparticles of any of claims 1 to 60 in a solvent;

b. dissolving a polymer in the solvent to form a solution or dispersion of the polymer and coated metal oxide nanoparticles; and

c. forming a film on a substrate.

110. The method of claim 109, wherein the forming step comprises at least one of spin coating, doctor blading, spray coating, drop casting, meniscus coating, or dip coating the solution or dispersion on a substrate, and removing or allowing the evaporation of the solvent, to form the film on the substrate.

111. The method of claim 109, wherein the forming step comprises printing, screen printing, or ink-jet printing.

112. The method of claim 109 or 110, wherein the polymer is an epoxy, a polyimide, a cyanate ester or polyurethane, a polyvinylidene difluoride, a fluoropolymer, a polyester, a polycarbonate, a polycarbonate-carbonate, a polyether-ketone, a polyphenylene oxide, or a polyphenylene sulfide, a polyvinylphenol, polyvinylpyrrolidinone, polyolefin, polyester, polyethylene naphthalate, cyanoethylated pullulan and other pulluan esters, siloxane polymers, and copolymers of a vinylidenefluoride or a trifluoroethylene or a chlorotrifluoroethylene or a hexafluoropropylene or copolymers thereof or mixtures thereof.

113. The method of claim 109 or 110, wherein the solvent is selected from N,N-dimethyl formamide, pyridine, N-methyl pyrrolidinone, chloroform, chlorobenzene, cyclohexane, methylehtyl ketone, methylisobutyl ketone, propyleneglycol methylether, propyleneglycol methylether acetate, o-xylene, decaline, and trichlorobenzene and mixtures thereof.

114. The film formed by the method of any of claims 109 to 113.

115. An article comprising the film of claim 114.

116. A film comprising the nanocomposite composition of any of claims 99 to 106.

117. A capacitor comprising the film of claim 114 or claim 116.

118. The capacitor of claim 117, wherein the film comprises two or more layers of the nanocomposite composition of any of claims 99 to 106.

119. The capacitor of claim 117, wherein the film has a dielectric constant of greater than about 19.

120. The capacitor of claim 117, wherein the film has a dielectric breakdown strength of greater than about 120 V/micrometer.

121. The capacitor of claim 117, wherein the film has an energy density of greater than about 3 J/cm^3.

122. The capacitor of claim 117, wherein the film has a dielectric constant of greater than about 19, a dielectric breakdown strength of greater than about 120 V/micrometer, and an energy density of greater than about 3 J/cm^3.