

ANIONIC FUNCTIONALIZED COLLOIDAL SILICA AND METHODS OF PRODUCTION

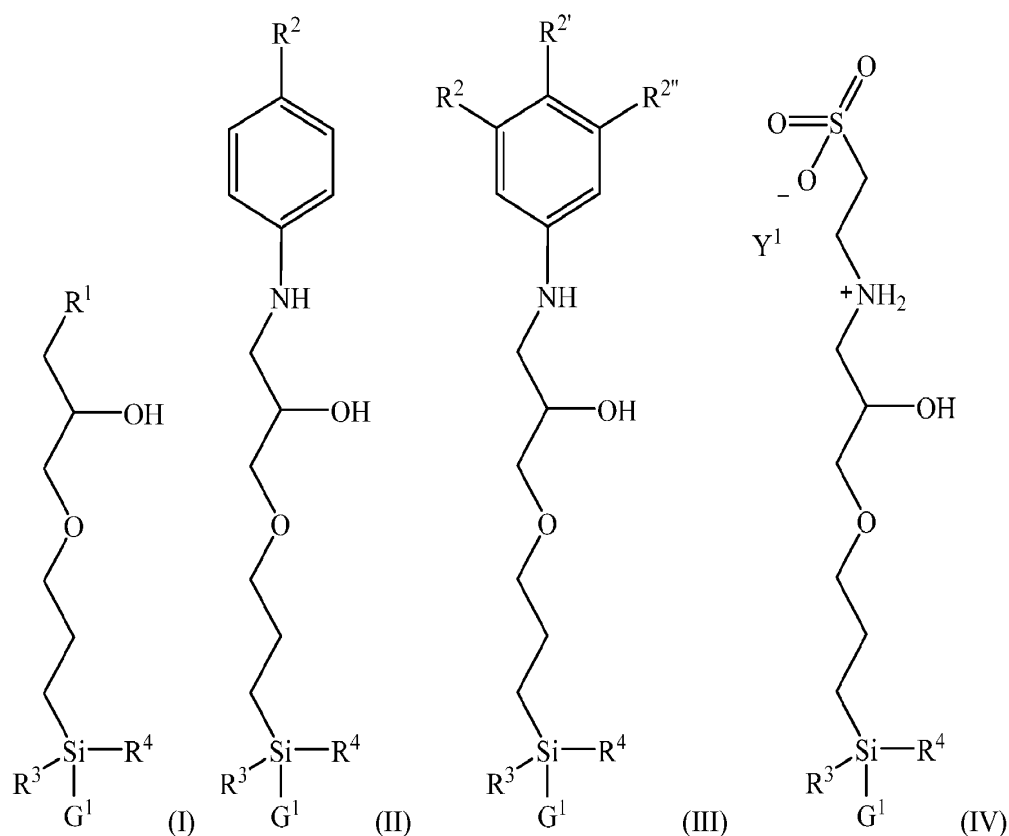
FIELD

[0001] The present technology relates generally to functionalized colloidal silica as well as methods useful for synthesizing such functionalized colloidal silica, including compositions that are stable to aging for 24 hours or longer at temperature of 80 °C when the composition includes a salt solution at an ionic strength of 0.5 to 3.0.

SUMMARY

[0002] In an aspect, the present technology provides a composition that includes water and a functionalized colloidal silica. The functionalized colloidal silica includes silica particles (where each silica particle includes a surface) and a structural unit according to

[0003] Formula I, a structural unit according to Formula II, a structural unit according to Formula III, or a structural unit according to Formula IV



where

R^1 is $-S-(CH_2)_nR^2$ or $-NH-NH-C(O)-(CH_2)_m-C(O)NH-NH_2$ where n is 1, 2, 3, 4, 5, or 6 and m is 1, 2, 3, 4, 5, 6, 7, or 8;

R^2 is independently at each occurrence $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$, $-CO_2H$, or $-CO_2^-$;

$R^{2'}$ and $R^{2''}$ are each independently H, $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$, $-CO_2H$, or $-CO_2^-$;

R^3 is hydroxyl, alkoxy, aryloxy, or G^2 ;

R^4 is hydroxyl, alkoxy, aryloxy, or G^3 ;

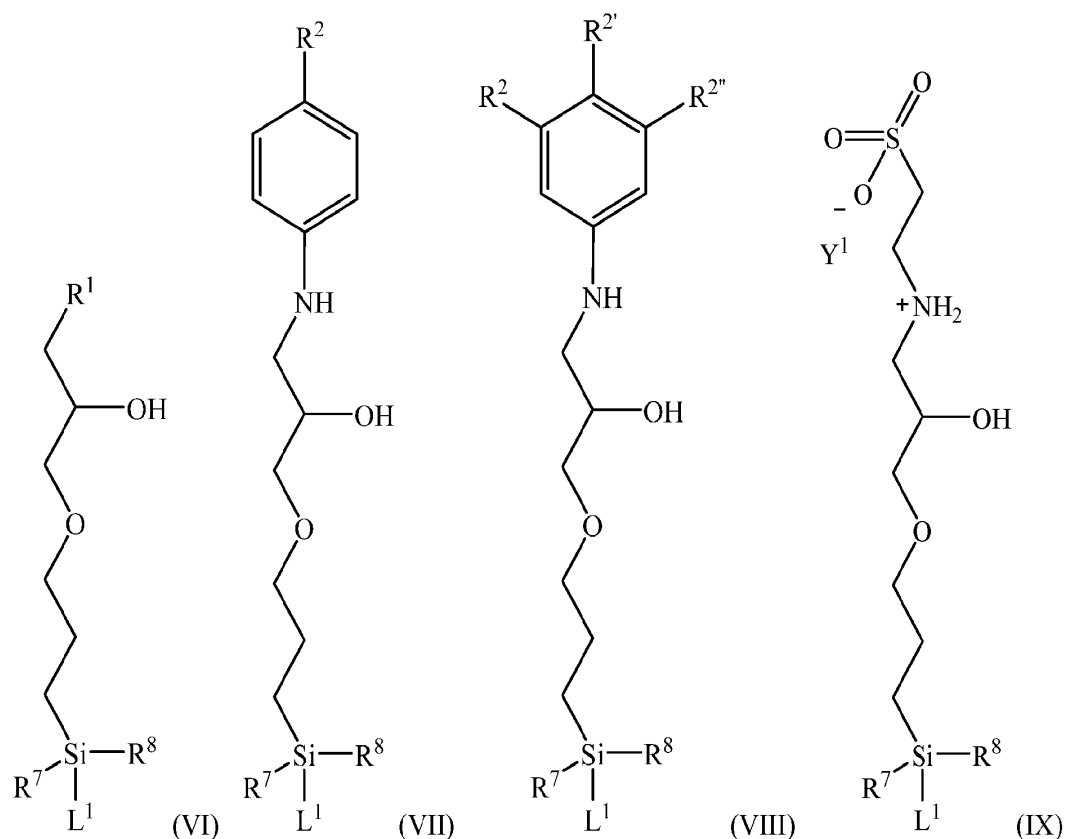
G^1 , G^2 , and G^3 are each independently an oxygen atom of the surface of the silica particle, where G^1 , G^2 , and G^3 are not the same oxygen atom;

Y^1 is independently at each occurrence a cation; and

Y^2 is independently at each occurrence a cation.

[0004] In another aspect, the present technology provides a method of making a functionalized colloidal silica (for example, a method of making a composition of any embodiment herein).

The method includes contacting a colloidal silica with a silane according to Formula VI, a silane according to Formula VII, a silane according to Formula VIII, or a silane according to Formula IX to yield the functionalized colloidal silica



where

R¹ is -S-(CH₂)_nR² or -NH-NH-C(O)-(CH₂)_m-C(O)NH-NH₂ where *n* is 1, 2, 3, 4, 5, or 6
and *m* is 1, 2, 3, 4, 5, 6, 7, or 8;

R² is independently at each occurrence -SO₃Y¹, -SO₃H, -SO₃⁻, -CO₂Y²,
-CO₂H, or -CO₂⁻;

R^{2'} and R^{2''} are each independently H, -SO₃Y¹, -SO₃H, -SO₃⁻, -CO₂Y², -CO₂H, or -CO₂⁻;

R⁷ is hydroxyl, alkoxy, or aryloxy;

R⁸ is hydroxyl, alkoxy, or aryloxy;

L¹ is alkoxy or aryloxy;

Y¹ is independently at each occurrence a cation; and

Y^2 is independently at each occurrence a cation.

[0005] In a further aspect, the present technology provides a functionalized silica prepared according to a method of any embodiment described herein.

[0006] It should be appreciated that all combinations of the foregoing concepts and additional concepts discussed in greater detail below (provided such concepts are not mutually inconsistent) are contemplated as being part of the subject matter disclosed herein. In particular, all combinations of claimed subject matter appearing at the end of this disclosure are contemplated as being part of the subject matter disclosed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1 provides a graph of pH vs. zeta potential of colloidal silica samples functionalized with different sulfonate groups and compared to unmodified colloidal silica.

[0008] FIG. 2 provides a graph of pH vs. zeta potential of sulfanilic acid modified and isophthalic acid modified colloidal silica as compared to unmodified HS-40.

[0009] FIG. 3 provides a graph of pH vs. zeta potential of hydrazide modified colloidal silica as compared to unmodified HS-40.

DETAILED DESCRIPTION

[0010] Various embodiments are described hereinafter. It should be noted that the specific embodiments are not intended as an exhaustive description or as a limitation to the broader aspects discussed herein. One aspect described in conjunction with a particular embodiment is not necessarily limited to that embodiment and can be practiced with any other embodiment(s).

[0011] As used herein and in the appended claims, singular articles such as “a” and “an” and “the” and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods

described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (*e.g.*, “such as”) provided herein, is intended merely to better illuminate the embodiments and does not pose a limitation on the scope of the claims unless otherwise stated. No language in the specification should be construed as indicating any non-claimed element as essential.

[0012] As used herein, “about” will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, “about” will mean up to plus or minus 10% of the particular term – for example, “about 10 wt. %” would be understood to mean “9 wt. % to 11 wt. %.” It is to be understood that when “about” precedes a term, the term is to be construed as disclosing “about” the term as well as the term without modification by “about” – for example, “about 10 wt. %” discloses “9 wt. % to 11 wt. %” as well as disclosing “10 wt. %.”

[0013] The phrase “and/or” as used in the present disclosure will be understood to mean any one of the recited members individually or a combination of any two or more thereof – for example, “A, B, and/or C” would mean “A or B or C; A and B; A and C; B and C; or the combination of A, B, and C.”

[0014] Generally, reference to a certain element such as hydrogen or H is meant to include all isotopes of that element. For example, if an R group is defined to include hydrogen or H, it also includes deuterium and tritium. Compounds comprising radioisotopes such as tritium, C¹⁴, P³² and S³⁵ are thus within the scope of the present technology. Procedures for inserting such labels into the compounds of the present technology will be readily apparent to those skilled in the art based on the disclosure herein.

[0015] In general, “substituted” refers to an organic group as defined below (*e.g.*, an alkyl group) in which one or more bonds to a hydrogen atom contained therein are replaced by a bond to non-hydrogen or non-carbon atoms. Substituted groups also include groups in which one or more bonds to a carbon(s) or hydrogen(s) atom are replaced by one or more bonds, including double or triple bonds, to a heteroatom. Thus, a substituted group is substituted with one or more

substituents, unless otherwise specified. In some embodiments, a substituted group is substituted with 1, 2, 3, 4, 5, or 6 substituents. Examples of substituent groups include: halogens (*i.e.*, F, Cl, Br, and I); hydroxyls; alkoxy, alkenoxy, aryloxy, aralkyloxy, heterocyclyl, heterocyclalkyl, heterocycloxy, and heterocyclalkoxy groups; carbonyls (oxo); carboxylates; esters; urethanes; oximes; hydroxylamines; alkoxyamines; aralkoxyamines; thiols; sulfides; sulfoxides; sulfones; sulfonyls; pentafluorosulfanyl (*i.e.*, SF₅), sulfonamides; amines; N-oxides; hydrazines; hydrazides; hydrazones; azides; amides; ureas; amidines; guanidines; enamines; imides; isocyanates; isothiocyanates; cyanates; thiocyanates; imines; nitro groups; and nitriles (*i.e.*, CN).

[0016] Substituted ring groups such as substituted cycloalkyl, aryl, heterocyclyl and heteroaryl groups also include rings and ring systems in which a bond to a hydrogen atom is replaced with a bond to a carbon atom. Therefore, substituted cycloalkyl, aryl, heterocyclyl and heteroaryl groups may also be substituted with substituted or unsubstituted alkyl, alkenyl, and alkynyl groups as defined below.

[0017] Alkyl groups include straight chain and branched chain alkyl groups having from 1 to 12 carbon atoms, and typically from 1 to 10 carbons or, in some embodiments, from 1 to 8, 1 to 6, or 1 to 4 carbon atoms. Alkyl groups may be substituted or unsubstituted. Examples of straight chain alkyl groups include groups such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, iso-butyl, sec-butyl, tert-butyl, neopentyl, isopentyl, and 2,2-dimethylpropyl groups. Representative substituted alkyl groups may be substituted one or more times with substituents such as those listed above, and include without limitation haloalkyl (e.g., trifluoromethyl), hydroxyalkyl, thioalkyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, alkoxyalkyl, carboxyalkyl, and the like.

[0018] Cycloalkyl groups include mono-, bi- or tricyclic alkyl groups having from 3 to 12 carbon atoms in the ring(s), or, in some embodiments, 3 to 10, 3 to 8, or 3 to 4, 5, or 6 carbon atoms. Cycloalkyl groups may be substituted or unsubstituted. Exemplary monocyclic cycloalkyl groups include, but not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl groups. In some embodiments, the cycloalkyl group has 3 to 8 ring members, whereas in other embodiments the number of ring carbon atoms range from 3 to 5, 3 to

6, or 3 to 7. Bi- and tricyclic ring systems include both bridged cycloalkyl groups and fused rings, such as, but not limited to, bicyclo[2.1.1]hexane, adamantyl, decalyl, and the like. Substituted cycloalkyl groups may be substituted one or more times with non-hydrogen and non-carbon groups as defined above. However, substituted cycloalkyl groups also include rings that are substituted with straight or branched chain alkyl groups as defined above. Representative substituted cycloalkyl groups may be mono-substituted or substituted more than once, such as, but not limited to, 2,2-, 2,3-, 2,4-, 2,5- or 2,6-disubstituted cyclohexyl groups, which may be substituted with substituents such as those listed above.

[0019] Cycloalkylalkyl groups are alkyl groups as defined above in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to a cycloalkyl group as defined above.

Cycloalkylalkyl groups may be substituted or unsubstituted. In some embodiments, cycloalkylalkyl groups have from 4 to 16 carbon atoms, 4 to 12 carbon atoms, and typically 4 to 10 carbon atoms. Substituted cycloalkylalkyl groups may be substituted at the alkyl, the cycloalkyl or both the alkyl and cycloalkyl portions of the group. Representative substituted cycloalkylalkyl groups may be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above.

[0020] Alkenyl groups include straight and branched chain alkyl groups as defined above, except that at least one double bond exists between two carbon atoms. Alkenyl groups may be substituted or unsubstituted. Alkenyl groups have from 2 to 12 carbon atoms, and typically from 2 to 10 carbons or, in some embodiments, from 2 to 8, 2 to 6, or 2 to 4 carbon atoms. In some embodiments, the alkenyl group has one, two, or three carbon-carbon double bonds. Examples include, but are not limited to vinyl, allyl, $-\text{CH}=\text{CH}(\text{CH}_3)$, $-\text{CH}=\text{C}(\text{CH}_3)_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_3)$, $-\text{C}(\text{CH}_2\text{CH}_3)=\text{CH}_2$, among others. Representative substituted alkenyl groups may be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above.

[0021] Cycloalkenyl groups include cycloalkyl groups as defined above, having at least one double bond between two carbon atoms. Cycloalkenyl groups may be substituted or unsubstituted. In some embodiments the cycloalkenyl group may have one, two or three double

bonds but does not include aromatic compounds. Cycloalkenyl groups have from 4 to 14 carbon atoms, or, in some embodiments, 5 to 14 carbon atoms, 5 to 10 carbon atoms, or even 5, 6, 7, or 8 carbon atoms. Examples of cycloalkenyl groups include cyclohexenyl, cyclopentenyl, cyclohexadienyl, cyclobutadienyl, and cyclopentadienyl.

[0022] Cycloalkenylalkyl groups are alkyl groups as defined above in which a hydrogen or carbon bond of the alkyl group is replaced with a bond to a cycloalkenyl group as defined above. Cycloalkenylalkyl groups may be substituted or unsubstituted. Substituted cycloalkenylalkyl groups may be substituted at the alkyl, the cycloalkenyl or both the alkyl and cycloalkenyl portions of the group. Representative substituted cycloalkenylalkyl groups may be substituted one or more times with substituents such as those listed above.

[0023] Alkynyl groups include straight and branched chain alkyl groups as defined above, except that at least one triple bond exists between two carbon atoms. Alkynyl groups may be substituted or unsubstituted. Alkynyl groups have from 2 to 12 carbon atoms, and typically from 2 to 10 carbons or, in some embodiments, from 2 to 8, 2 to 6, or 2 to 4 carbon atoms. In some embodiments, the alkynyl group has one, two, or three carbon-carbon triple bonds. Examples include, but are not limited to $-\text{C}\equiv\text{CH}$, $-\text{C}\equiv\text{CCH}_3$, $-\text{CH}_2\text{C}\equiv\text{CCH}_3$, and $-\text{C}\equiv\text{CCH}_2\text{CH}(\text{CH}_2\text{CH}_3)_2$, among others. Representative substituted alkynyl groups may be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above.

[0024] Aryl groups are cyclic aromatic hydrocarbons that do not contain heteroatoms. Aryl groups herein include monocyclic, bicyclic, and tricyclic ring systems. Aryl groups may be substituted or unsubstituted. Thus, aryl groups include, but are not limited to, phenyl, azulenyl, heptalenyl, biphenyl, fluorenyl, phenanthrenyl, anthracenyl, indenyl, indanyl, pentalenyl, and naphthyl groups. In some embodiments, aryl groups contain 6-14 carbons, and in others from 6 to 12 or even 6-10 carbon atoms in the ring portions of the groups. In some embodiments, the aryl groups are phenyl or naphthyl. The phrase “aryl groups” includes groups containing fused rings, such as fused aromatic-aliphatic ring systems (e.g., indanyl, tetrahydronaphthyl, and the like). Representative substituted aryl groups may be mono-substituted (e.g., tolyl) or substituted more than once. For example, monosubstituted aryl groups include, but are not limited to, 2-, 3-,

4-, 5-, or 6-substituted phenyl or naphthyl groups, which may be substituted with substituents such as those listed above.

[0025] Aralkyl groups are alkyl groups as defined above in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to an aryl group as defined above. Aralkyl groups may be substituted or unsubstituted. In some embodiments, aralkyl groups contain 7 to 16 carbon atoms, 7 to 14 carbon atoms, or 7 to 10 carbon atoms. Substituted aralkyl groups may be substituted at the alkyl, the aryl or both the alkyl and aryl portions of the group. Representative aralkyl groups include but are not limited to benzyl and phenethyl groups and fused (cycloalkylaryl)alkyl groups such as 4-indanylethyl. Representative substituted aralkyl groups may be substituted one or more times with substituents such as those listed above.

[0026] Heterocyclyl groups include aromatic (also referred to as heteroaryl) and non-aromatic ring compounds containing 3 or more ring members, of which one or more is a heteroatom such as, but not limited to, N, O, and S. Heterocyclyl groups may be substituted or unsubstituted. In some embodiments, the heterocyclyl group contains 1, 2, 3 or 4 heteroatoms. In some embodiments, heterocyclyl groups include mono-, bi- and tricyclic rings having 3 to 16 ring members, whereas other such groups have 3 to 6, 3 to 10, 3 to 12, or 3 to 14 ring members. Heterocyclyl groups encompass aromatic, partially unsaturated, and saturated ring systems, such as, for example, imidazolyl, imidazolynyl and imidazolidynyl groups. The phrase “heterocyclyl group” includes fused ring species including those comprising fused aromatic and non-aromatic groups, such as, for example, benzotriazolyl, 2,3-dihydrobenzo[1,4]dioxynyl, and benzo[1,3]dioxolyl. The phrase also includes bridged polycyclic ring systems containing a heteroatom such as, but not limited to, quinuclidyl. The phrase includes heterocyclyl groups that have other groups, such as alkyl, oxo or halo groups, bonded to one of the ring members, referred to as “substituted heterocyclyl groups.” Heterocyclyl groups include, but are not limited to, aziridinyl, azetidynyl, pyrrolidinyl, imidazolidynyl, pyrazolidynyl, thiazolidynyl, tetrahydrothiophenyl, tetrahydrofuranyl, dioxolyl, furanyl, thiophenyl, pyrrolyl, pyrrolinyl, imidazolyl, imidazolynyl, pyrazolyl, pyrazolynyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, thiazolynyl, isothiazolyl, thiadiazolyl, oxadiazolyl, piperidyl, piperazinyl, morpholinyl, thiomorpholinyl, tetrahydropyranyl, tetrahydrothiopyranyl, oxathiane, dioxyl, dithianyl, pyranyl, pyridyl, pyrimidinyl, pyridazinyl, pyrazinyl, triazinyl, dihydropyridyl, dihydrodithiinyl,

dihydrodithionyl, homopiperazinyl, quinuclidyl, indolyl, indolinyl, isoindolyl, azaindolyl (pyrrolopyridyl), indazolyl, indoliziny, benzotriazolyl, benzimidazolyl, benzofuranyl, benzothiophenyl, benzthiazolyl, benzoxadiazolyl, benzoxazinyl, benzodithiiny, benzoxathiiny, benzothiazinyl, benzoxazolyl, benzothiazolyl, benzothiadiaazolyl, benzo[1,3]dioxolyl, pyrazolopyridyl, imidazopyridyl (azabenzimidazolyl), triazolopyridyl, isoxazolopyridyl, purinyl, xanthinyl, adeninyl, guaninyl, quinolinyl, isoquinolinyl, quinoliziny, quinoxalinyl, quinazoliny, cinnolinyl, phthalazinyl, naphthyridinyl, pteridinyl, thianaphthyl, dihydrobenzothiazinyl, dihydrobenzofuranyl, dihydroindolyl, dihydrobenzodioxinyl, tetrahydroindolyl, tetrahydroindazolyl, tetrahydrobenzimidazolyl, tetrahydrobenzotriazolyl, tetrahydropyrrolopyridyl, tetrahydropyrazolopyridyl, tetrahydroimidazopyridyl, tetrahydrotriazolopyridyl, and tetrahydroquinolinyl groups. Representative substituted heterocyclyl groups may be mono-substituted or substituted more than once, such as, but not limited to, pyridyl or morpholinyl groups, which are 2-, 3-, 4-, 5-, or 6-substituted, or disubstituted with various substituents such as those listed above.

[0027] Heteroaryl groups are aromatic ring compounds containing 5 or more ring members, of which, one or more is a heteroatom such as, but not limited to, N, O, and S. Heteroaryl groups may be substituted or unsubstituted. Heteroaryl groups include, but are not limited to, groups such as pyrrolyl, pyrazolyl, triazolyl, tetrazolyl, oxazolyl, isoxazolyl, thiazolyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl, thiophenyl, benzothiophenyl, furanyl, benzofuranyl, indolyl, azaindolyl (pyrrolopyridinyl), indazolyl, benzimidazolyl, imidazopyridinyl (azabenzimidazolyl), pyrazolopyridinyl, triazolopyridinyl, benzotriazolyl, benzoxazolyl, benzothiazolyl, benzothiadiaazolyl, imidazopyridinyl, isoxazolopyridinyl, thianaphthyl, purinyl, xanthinyl, adeninyl, guaninyl, quinolinyl, isoquinolinyl, tetrahydroquinolinyl, quinoxalinyl, and quinazoliny groups. Heteroaryl groups include fused ring compounds in which all rings are aromatic such as indolyl groups and include fused ring compounds in which only one of the rings is aromatic, such as 2,3-dihydro indolyl groups. Representative substituted heteroaryl groups may be substituted one or more times with various substituents such as those listed above.

[0028] Heterocyclylalkyl groups are alkyl groups as defined above in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to a heterocyclyl group as defined above. Heterocyclylalkyl groups may be substituted or unsubstituted. Substituted heterocyclylalkyl

groups may be substituted at the alkyl, the heterocyclyl or both the alkyl and heterocyclyl portions of the group. Representative heterocyclyl alkyl groups include, but are not limited to, morpholin-4-yl-ethyl, furan-2-yl-methyl, imidazol-4-yl-methyl, pyridin-3-yl-methyl, tetrahydrofuran-2-yl-ethyl, and indol-2-yl-propyl. Representative substituted heterocyclylalkyl groups may be substituted one or more times with substituents such as those listed above.

[0029] Heteroaralkyl groups are alkyl groups as defined above in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to a heteroaryl group as defined above. Heteroaralkyl groups may be substituted or unsubstituted. Substituted heteroaralkyl groups may be substituted at the alkyl, the heteroaryl or both the alkyl and heteroaryl portions of the group. Representative substituted heteroaralkyl groups may be substituted one or more times with substituents such as those listed above.

[0030] Groups described herein having two or more points of attachment (i.e., divalent, trivalent, or polyvalent) within the compound of the present technology are designated by use of the suffix, “ene.” For example, divalent alkyl groups are alkylene groups, divalent aryl groups are arylene groups, divalent heteroaryl groups are divalent heteroarylene groups, and so forth. Substituted groups having a single point of attachment to the compound of the present technology are not referred to using the “ene” designation. Thus, e.g., chloroethyl is not referred to herein as chloroethylene.

[0031] Alkoxy groups are hydroxyl groups (-OH) in which the bond to the hydrogen atom is replaced by a bond to a carbon atom of a substituted or unsubstituted alkyl group as defined above. Alkoxy groups may be substituted or unsubstituted. Examples of linear alkoxy groups include but are not limited to methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, and the like. Examples of branched alkoxy groups include but are not limited to isopropoxy, sec-butoxy, tert-butoxy, isopentoxy, isohexoxy, and the like. Examples of cycloalkoxy groups include but are not limited to cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, and the like. Representative substituted alkoxy groups may be substituted one or more times with substituents such as those listed above.

[0032] The terms “alkanoyl” and “alkanoyloxy” as used herein can refer, respectively, to $-C(O)-$ alkyl groups and $-O-C(O)-$ alkyl groups, each containing 2–5 carbon atoms. Similarly, “aryloyl” and “aryloyloxy” refer to $-C(O)-$ aryl groups and $-O-C(O)-$ aryl groups.

[0033] The terms “aryloxy” and “arylalkoxy” refer to, respectively, a substituted or unsubstituted aryl group bonded to an oxygen atom and a substituted or unsubstituted aralkyl group bonded to the oxygen atom at the alkyl. Examples include but are not limited to phenoxy, naphthyloxy, and benzyloxy. Representative substituted aryloxy and arylalkoxy groups may be substituted one or more times with substituents such as those listed above.

[0034] The term “carboxylate” as used herein refers to a $-COOH$ group.

[0035] The term “ester” as used herein refers to $-COOR^{70}$ and $-C(O)O-G$ groups. R^{70} is a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl, aralkyl, heterocyclylalkyl or heterocyclyl group as defined herein. G is a carboxylate protecting group. Carboxylate protecting groups are well known to one of ordinary skill in the art. An extensive list of protecting groups for the carboxylate group functionality may be found in Protective Groups in Organic Synthesis, Greene, T.W.; Wuts, P. G. M., John Wiley & Sons, New York, NY, (3rd Edition, 1999) which can be added or removed using the procedures set forth therein and which is hereby incorporated by reference in its entirety and for any and all purposes as if fully set forth herein.

[0036] The term “amide” (or “amido”) includes C- and N-amide groups, i.e., $-C(O)NR^{71}R^{72}$, and $-NR^{71}C(O)R^{72}$ groups, respectively. R^{71} and R^{72} are independently hydrogen, or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, heterocyclylalkyl or heterocyclyl group as defined herein. Amido groups therefore include but are not limited to carbamoyl groups ($-C(O)NH_2$) and formamide groups ($-NHC(O)H$). In some embodiments, the amide is $-NR^{71}C(O)-(C_{1-5} \text{ alkyl})$ and the group is termed “carbonylamino,” and in others the amide is $-NHC(O)-$ alkyl and the group is termed “alkanoylamino.”

[0037] The term “nitrile” or “cyano” as used herein refers to the $-CN$ group.

[0038] Urethane groups include N- and O-urethane groups, i.e., $-NR^{73}C(O)OR^{74}$ and $-OC(O)NR^{73}R^{74}$ groups, respectively. R^{73} and R^{74} are independently a substituted or

unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, heterocyclalkyl, or heterocycl group as defined herein. R^{73} may also be H.

[0039] The term “amine” (or “amino”) as used herein refers to $-NR^{75}R^{76}$ groups, wherein R^{75} and R^{76} are independently hydrogen, or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, heterocyclalkyl or heterocycl group as defined herein. In some embodiments, the amine is alkylamino, dialkylamino, arylamino, or alkylarylamino. In other embodiments, the amine is NH_2 , methylamino, dimethylamino, ethylamino, diethylamino, propylamino, isopropylamino, phenylamino, or benzylamino.

[0040] The term “sulfonamido” includes S- and N-sulfonamide groups, i.e., $-SO_2NR^{78}R^{79}$ and $-NR^{78}SO_2R^{79}$ groups, respectively. R^{78} and R^{79} are independently hydrogen, or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, heterocyclalkyl, or heterocycl group as defined herein. Sulfonamido groups therefore include but are not limited to sulfamoyl groups ($-SO_2NH_2$). In some embodiments herein, the sulfonamido is $-NHSO_2$ -alkyl and is referred to as the “alkylsulfonylamino” group.

[0041] The term “thiol” refers to $-SH$ groups, while “sulfides” include $-SR^{80}$ groups, “sulfoxides” include $-S(O)R^{81}$ groups, “sulfones” include $-SO_2R^{82}$ groups, and “sulfonyls” include $-SO_2OR^{83}$. R^{80} , R^{81} , R^{82} , and R^{83} are each independently a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl aralkyl, heterocycl or heterocyclalkyl group as defined herein. In some embodiments the sulfide is an alkylthio group, $-S$ -alkyl. The term “sulfonic acid” as used herein refers to a $-SO_3H$ group, and “sulfonate” as used herein refers to a $-SO_3^-$ group (a deprotonated form of sulfonic acid).

[0042] The term “urea” refers to $-NR^{84}-C(O)-NR^{85}R^{86}$ groups. R^{84} , R^{85} , and R^{86} groups are independently hydrogen, or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, heterocycl, or heterocyclalkyl group as defined herein.

[0043] The term “amidine” refers to $-C(NR^{87})NR^{88}R^{89}$ and $-NR^{87}C(NR^{88})R^{89}$, wherein R^{87} , R^{88} , and R^{89} are each independently hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl aralkyl, heterocycl or heterocyclalkyl group as defined herein.

[0044] The term “guanidine” refers to $-\text{NR}^{90}\text{C}(\text{NR}^{91})\text{NR}^{92}\text{R}^{93}$, wherein R^{90} , R^{91} , R^{92} and R^{93} are each independently hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl aralkyl, heterocyclyl or heterocyclylalkyl group as defined herein.

[0045] The term “enamine” refers to $-\text{C}(\text{R}^{94})=\text{C}(\text{R}^{95})\text{NR}^{96}\text{R}^{97}$ and $-\text{NR}^{94}\text{C}(\text{R}^{95})=\text{C}(\text{R}^{96})\text{R}^{97}$, wherein R^{94} , R^{95} , R^{96} and R^{97} are each independently hydrogen, a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl aralkyl, heterocyclyl or heterocyclylalkyl group as defined herein.

[0046] The term “halogen” or “halo” as used herein refers to bromine, chlorine, fluorine, or iodine. In some embodiments, the halogen is fluorine. In other embodiments, the halogen is chlorine or bromine.

[0047] The term “hydroxyl” as used herein can refer to $-\text{OH}$ or its ionized form, $-\text{O}^-$. A “hydroxyalkyl” group is a hydroxyl-substituted alkyl group, such as $\text{HO}-\text{CH}_2-$.

[0048] The term “imide” refers to $-\text{C}(\text{O})\text{NR}^{98}\text{C}(\text{O})\text{R}^{99}$, wherein R^{98} and R^{99} are each independently hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl aralkyl, heterocyclyl or heterocyclylalkyl group as defined herein.

[0049] The term “imine” refers to $-\text{CR}^{100}(\text{NR}^{101})$ and $-\text{N}(\text{CR}^{100}\text{R}^{101})$ groups, wherein R^{100} and R^{101} are each independently hydrogen or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl aralkyl, heterocyclyl or heterocyclylalkyl group as defined herein, with the proviso that R^{100} and R^{101} are not both simultaneously hydrogen.

[0050] The term “nitro” as used herein refers to an $-\text{NO}_2$ group.

[0051] The term “trifluoromethyl” as used herein refers to $-\text{CF}_3$.

[0052] The term “trifluoromethoxy” as used herein refers to $-\text{OCF}_3$.

[0053] The term “azido” refers to $-\text{N}_3$.

[0054] The term “trialkyl ammonium” refers to a $-\text{N}(\text{alkyl})_3$ group. A trialkylammonium group is positively charged and thus typically has an associated anion, such as halogen anion.

[0055] The term “isocyano” refers to –NC.

[0056] The term “isothiocyano” refers to –NCS.

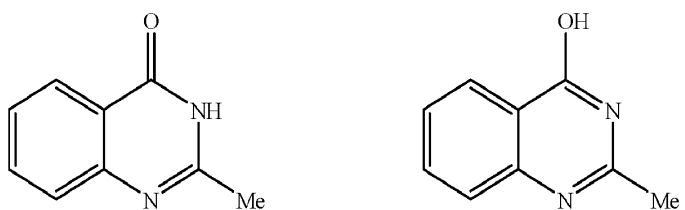
[0057] The term “pentafluorosulfanyl” refers to –SF₅.

[0058] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 atoms refers to groups having 1, 2, or 3 atoms. Similarly, a group having 1-5 atoms refers to groups having 1, 2, 3, 4, or 5 atoms, and so forth.

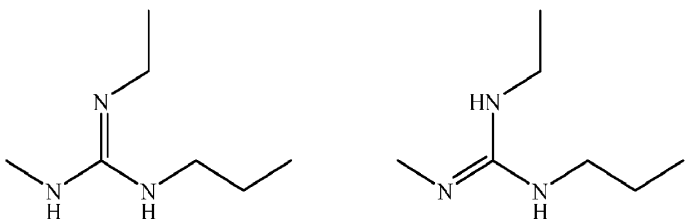
[0059] As understood by one of ordinary skill in the art, “molecular weight” (also known as “relative molar mass”) is a dimensionless quantity but is converted to molar mass by multiplying by 1 gram/mole or by multiplying by 1 Da – for example, a compound with a weight-average molecular weight of 5,000 has a weight-average molar mass of 5,000 g/mol and a weight-average molar mass of 5,000 Da.

[0060] Those of skill in the art will appreciate that compounds of the present technology may exhibit the phenomena of tautomerism, conformational isomerism, geometric isomerism, and/or stereoisomerism. As the formula drawings within the specification and claims can represent only one of the possible tautomeric, conformational isomeric, stereochemical or geometric isomeric forms, it should be understood that the present technology encompasses any tautomeric, conformational isomeric, stereochemical and/or geometric isomeric forms of the compounds having one or more of the utilities described herein, as well as mixtures of these various different forms.

[0061] “Tautomers” refers to isomeric forms of a compound that are in equilibrium with each other. The presence and concentrations of the isomeric forms will depend on the environment the compound is found in and may be different depending upon, for example, whether the compound is a solid or is in an organic or aqueous solution. For example, in aqueous solution, quinazolinones may exhibit the following isomeric forms, which are referred to as tautomers of each other:



[0062] As another example, guanidines may exhibit the following isomeric forms in protic organic solution, also referred to as tautomers of each other:



[0063] Because of the limits of representing compounds by structural formulas, it is to be understood that all chemical formulas of the compounds described herein represent all tautomeric forms of compounds and are within the scope of the present technology.

[0064] Stereoisomers of compounds (also known as optical isomers) include all chiral, diastereomeric, and racemic forms of a structure, unless the specific stereochemistry is expressly indicated. Thus, compounds used in the present technology include enriched or resolved optical isomers at any or all asymmetric atoms as are apparent from the depictions. Both racemic and diastereomeric mixtures, as well as the individual optical isomers can be isolated or synthesized so as to be substantially free of their enantiomeric or diastereomeric partners, and these stereoisomers are all within the scope of the present technology.

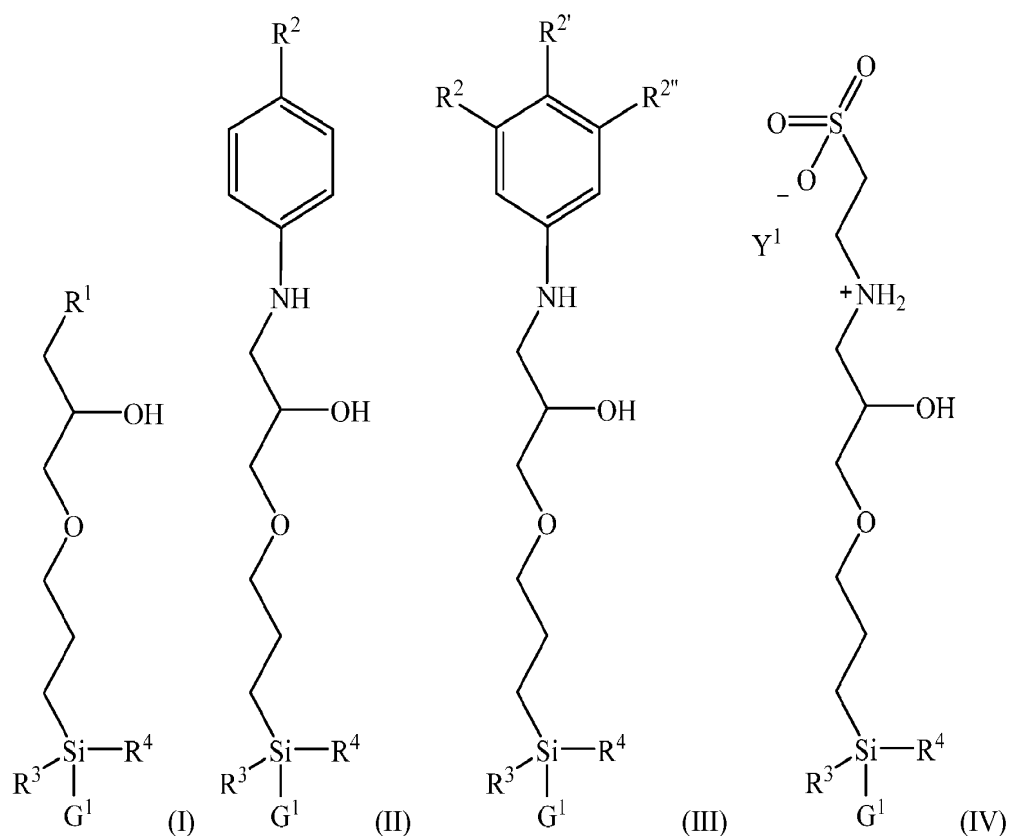
[0065] The compounds of the present technology may exist as solvates, especially hydrates. Hydrates may form during manufacture of the compounds or compositions comprising the compounds, or hydrates may form over time due to the hygroscopic nature of the compounds. Compounds of the present technology may exist as organic solvates as well, including DMF, ether, and alcohol solvates, among others. The identification and preparation of any particular solvate is within the skill of the ordinary artisan of synthetic organic chemistry.

The Present Technology

[0066] For colloidal silica to be used under extreme conditions (*e.g.*, high divalent metal salt solutions, high trivalent metal salt solutions, wide pH range, and/or high temperatures) with applications such as enhanced oil recovery, metal surface treatments, and electroplating formulations, colloidal stability is a more stringent requirement. Indeed, as shown by the Comparative Examples disclosed herein, functionalized colloidal silica available prior to the present disclosure suffers stability issues in such extreme conditions.

[0067] In addition, colloidal silica particles have been used in coating or paint formulations, such as described in U.S. Pat. Nos. 8,436,088, 9,598,557, and 10,487,240. In paint formulations, especially in aqueous systems that contain latex binder particles, various components are present and the components such as surfactants, coalescent agents, defoamers, thickeners, etc., may undesirably interact with unmodified colloidal silica and affect the stability of the colloidal system.

[0068] The present technology addresses the above-discussed deficiencies—including in relation to enhanced oil recovery, metal surface treatments (*e.g.*, anticorrosion metal surface treatments), electroplating, and coatings—as well as provides additional advantages. Thus, in an aspect, the present technology provides a composition that includes water and a functionalized colloidal silica. The functionalized colloidal silica includes silica particles (where each silica particle includes a surface) and a structural unit according to Formula I, a structural unit according to Formula II, a structural unit according to Formula III, or a structural unit according to Formula IV,



wherein

R¹ is -S-(CH₂)_nR² or -NH-NH-C(O)-(CH₂)_m-C(O)NH-NH₂ where *n* is 1, 2, 3, 4, 5, or 6 and *m* is 1, 2, 3, 4, 5, 6, 7, or 8;

R² is independently at each occurrence -SO₃Y¹, -SO₃H, -SO₃⁻, -CO₂Y², -CO₂H, or -CO₂⁻;

R^{2'} and R^{2''} are each independently H, -SO₃Y¹, -SO₃H, -SO₃⁻, -CO₂Y², -CO₂H, or -CO₂⁻;

R³ is hydroxyl, alkoxy, aryloxy, or G²;

R⁴ is hydroxyl, alkoxy, aryloxy, or G³;

G¹, G², and G³ are each independently an oxygen atom of the surface of the silica particle, where G¹, G², and G³ are not the same oxygen atom;

Y¹ is independently at each occurrence a cation; and

Y² is independently at each occurrence a cation.

[0069] The composition may include a pH of about 2 to about 11 or a pH of about 3.5 to about

11. The composition may include a pH of about 11 or lower; thus, the composition herein may

include a pH of about 3.5, about 4.0, about 4.5, about 5.0, about 5.5, about 6.0, about 6.5, about 7.0, about 7.5, about 8.0, about 8.5, about 9.0, about 9.5, about 10.0, about 10.5, about 11.0, or any range including and/or in-between any two of these values.

[0070] In any embodiment where the composition includes a pH of about 3.5 to 11, the functionalized colloidal silica may include a negative zeta potential. The negative zeta potential of any such embodiment herein may be about -1 millivolt ("mV"), about -2 mV, about -3 mV, about -4 mV, about -5 mV, about -6 mV, about -7 mV, about -8 mV, about -9 mV, about -10 mV, about -15 mV, about -20 mV, about -25 mV, about -30 mV, about -35 mV, about -40 mV, about -45 mV, about -50 mV, about -55 mV, about -60 mV, about -65 mV, about -70 mV, or any range including and/or in-between any two of these values. In any embodiment where the composition includes a pH of about 3.5 to 11, the functionalized colloidal silica may include a zeta potential of about -50 mV to about -60 mV.

[0071] In any embodiment, where the composition includes a pH of about 11 or lower, the composition may include a molar ratio of any of the structural units according to Formulas I-IV to any other of the structural units according to Formulas I-IV (*i.e.*, [moles of structural units according to one formula] / [moles of structural units according to another formula]) of about 1:1 or greater. Thus, in any embodiment where the composition includes a pH of about 11 or lower, the composition may include a molar ratio of any one of the structural units according to one of Formulas I-IV to structural units according to any other of the structural units according to Formulas I-IV of about 1:1, about 2:1, about 3:1, about 4:1, about 5:1, about 6:1, about 7:1, about 8:1, about 9:1, about 10:1, about 20:1, about 30:1, about 40:1, about 50:1, about 100:1, about 1,000:1, a range greater than any one of these value, or any range including and/or in-between any two of these values.

[0072] In any embodiment herein, the silica particles may have a median diameter as determined by dynamic light scattering or disc centrifuge analysis of about 1 nm to about 100 nm (D50 on a volume basis). Thus, the median diameter of the silica particles as determined by dynamic light scattering may be about 1 nm, about 5 nm, about 10 nm, about 15 nm, about 20 nm, about 25 nm, about 30 nm, about 35 nm, about 40 nm, about 45 nm, about 50 nm, about 55 nm, about 60

nm, about 65 nm, about 70 nm, about 75 nm, about 80 nm, about 85 nm, about 90 nm, about 95 nm, about 100 nm, or any range including and/or in-between any two of these values.

[0073] In any embodiment herein, the silica particles may have a Sears surface area of about 25 m²/g to about 1,200 m²/g. See Sears, "Determination of Specific Area of Colloidal Silica by Titration with Sodium Hydroxide" *Analytical Chemistry* **1956**, 28(12), 1981-1983

<https://doi.org/10.1021/ac60120a048>. Thus, the silica particles of any embodiment herein may have a Sears surface area of about 25 m²/g, 26 m²/g, 27 m²/g, 28 m²/g, 29 m²/g, 30 m²/g, 35 m²/g, 40 m²/g, 45 m²/g, 50 m²/g, 55 m²/g, 60 m²/g, 70 m²/g, 80 m²/g, 90 m²/g, 100 m²/g, 150 m²/g, 200 m²/g, 250 m²/g, 300 m²/g, 350 m²/g, 400 m²/g, 450 m²/g, 500 m²/g, 550 m²/g, 600 m²/g, 650 m²/g, 700 m²/g, 750 m²/g, 800 m²/g, 850 m²/g, 900 m²/g, 950 m²/g, 1,000 m²/g, 1,100 m²/g, 1,200 m²/g, or any range including and/or in-between any two of these values.

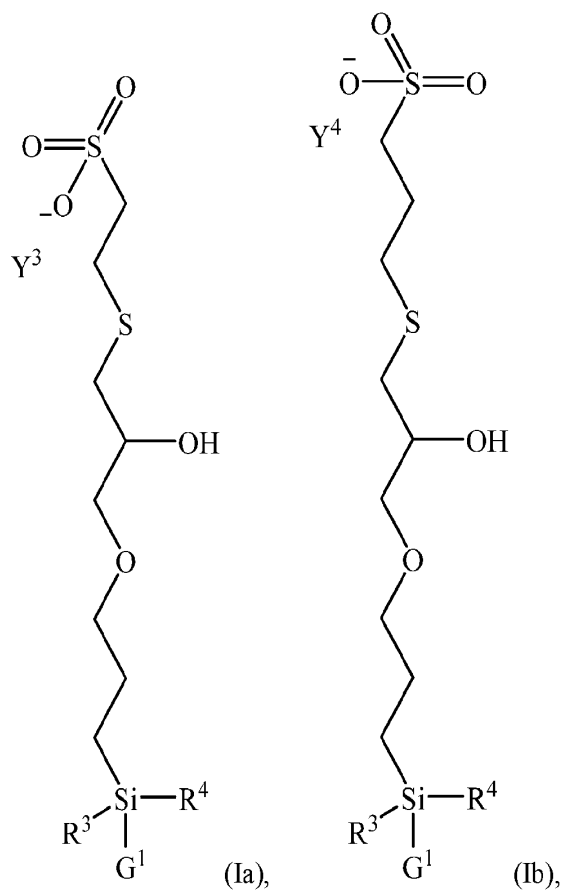
[0074] The composition of any embodiment herein may include a number of structural units according to Formula I, structural units according to Formula II, structural units according to Formula III, and/or structural units according to Formula IV per nm² surface area of about 0.8 to about 3.5. Accordingly, the composition of any embodiment herein may include a number of structural units according to Formula I, structural units according to Formula II, structural units according to Formula III, and/or structural units according to Formula IV per nm² surface area of about 0.8, about 0.9, about 1.0, about 1.1, about 1.2, about 1.3, about 1.4, about 1.5, about 1.6, about 1.7, about 1.8, about 1.9, about 2.0, about 2.1, about 2.2, about 2.3, about 2.4, about 2.5, about 2.6, about 2.7, about 2.8, about 2.9, about 3.0, about 3.1, about 3.2, about 3.3, about 3.4, about 3.5, or any range including and/or in-between any two of these values.

[0075] The composition of any embodiment herein may include a mass percentage composition of carbon as determined by elemental analysis of about 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, or any range including and/or between any two of these values.

[0076] The composition of any embodiment including structural units with sulfur may include a percentage composition of sulfur as determined by elemental analysis of about 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, or any range including and/or between any two of these values.

[0077] The composition of any embodiment including structural units with nitrogen may include a percentage composition of nitrogen as determined by elemental analysis of about 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, or any range including and/or between any two of these values.

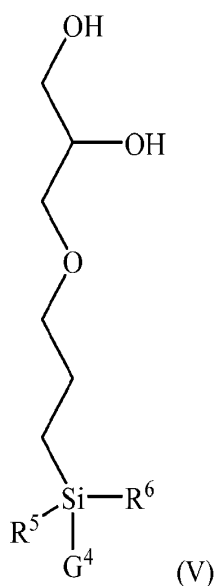
[0078] In any embodiment herein, it may be that the composition includes a structural unit according to Formula I and R^1 is $-(CH_2)_2SO_3Na$ and/or R^1 is $-(CH_2)_3SO_3Na$. In any embodiment herein, it may be that the composition includes a structural unit according to Formula I and R^1 is $-NH-NH-C(O)-(CH_2)_4-C(O)NH-NH_2$. In any embodiment herein, it may be that the composition includes a structural unit according to Formula II and R^2 is $-SO_3Na$. In any embodiment herein, it may be that the composition includes a structural unit according to Formula III where R^2 is $-SO_3Na$ and $R^{2'}$ and $R^{2''}$ are each independently H. In any embodiment herein, it may be that the composition includes a structural unit according to Formula III where R^2 is $-CO_2H$, $R^{2'}$ is H, and $R^{2''}$ is $-CO_2H$. In any embodiment herein, it may be that the composition includes a structural unit according to Formula III where R^2 is $-CO_2H$, $R^{2'}$ is $-CO_2H$, and $R^{2''}$ is H. In any embodiment herein, it may be that the composition includes a structural unit according to Formula III where R^2 is $-CO_2H$, $R^{2'}$ is $-CO_2H$, and $R^{2''}$ is $-CO_2H$. In any embodiment herein, it may be that the composition includes a structural unit according to Formula IV. In any embodiment herein, it may be that R^3 is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G^2 . In any embodiment herein, it may be that it may be that R^4 is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G^3 . In any embodiment herein, it may be that R^3 is G^2 . In any embodiment herein, it may be that R^4 is hydroxyl. In any embodiment herein, the silica particles may include at least one structural unit according to Formula Ia or Ib



where Y³ and Y⁴ are independently at each occurrence a cation.

[0079] In any embodiment herein, Y¹, Y², Y³, and Y⁴ may independently at each occurrence be, for example, NH₄⁺, Na⁺, Li⁺, K⁺, Ag⁺, Ca²⁺, Mg²⁺, or Zn²⁺.

[0080] In any embodiment herein, it may be that the silica particles further include at least one structural unit according to Formula V



wherein

R^5 is hydroxyl, alkoxy, aryloxy, or G^5 ;

R^6 is hydroxyl, alkoxy, aryloxy, or G^6 ;

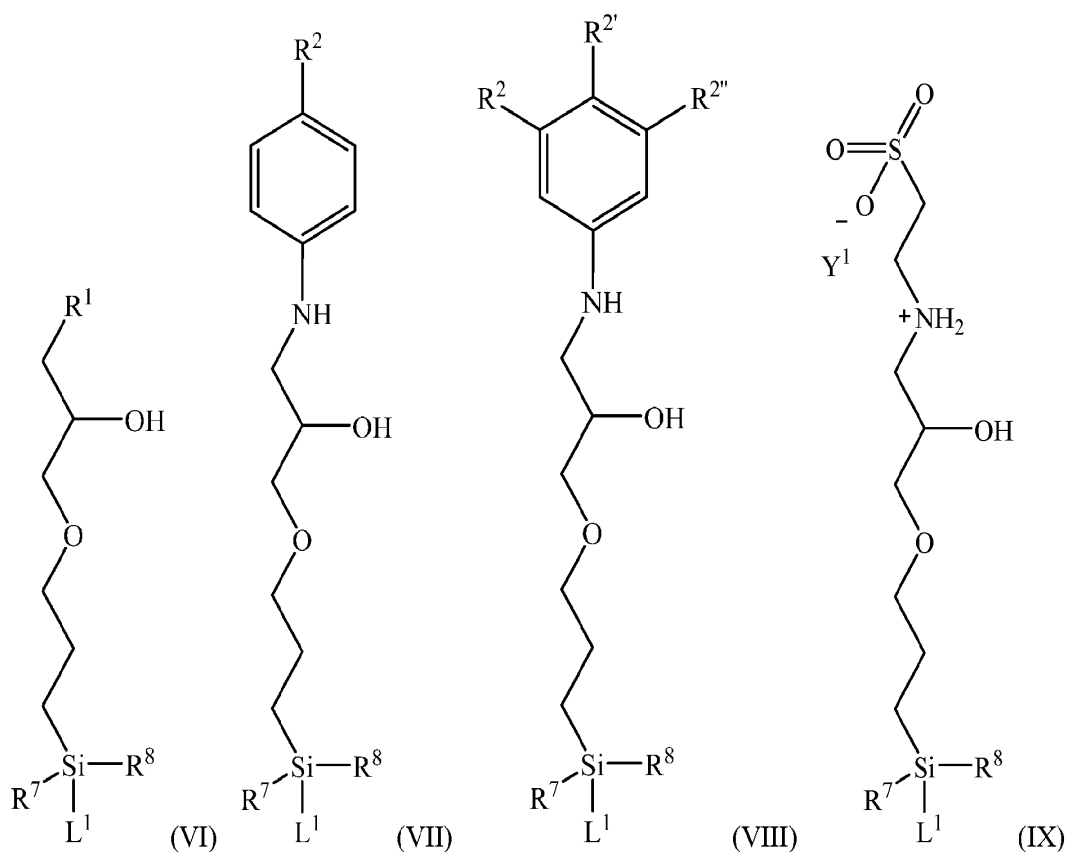
G^4 , G^5 , and G^6 are each independently an oxygen atom of the surface of the silica particle, where G^4 , G^5 , and G^6 are not the same oxygen atom.

[0081] In any embodiment herein, it may be that R^4 is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G^5 . In any embodiment herein, it may be that it may be that R^5 is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G^6 .

[0082] The composition of any embodiment herein may include about 0.1 wt% to about 50 wt% of the functionalized colloidal silica. Thus, in any embodiment herein the composition may include the functionalized colloidal silica in an amount of about 0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt%, 0.9 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt%, 9 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, 45 wt%, 50 wt%, or any range including and/or in-between any two of these values. For example, in any embodiment herein the composition may include the functionalized colloidal silica in an amount of about 0.1 wt% to about 30 wt%, about 5 wt% to about 30 wt%, about 10 wt% to about 30 wt%, or about 0.1 wt% to about 5 wt%.

[0083] The composition of any embodiment herein may be stable to aging for 24 hours or longer at temperature of 80 °C when the composition comprises a salt solution at an ionic strength of 0.5 to 3.0. The salt solution of any embodiment herein may include NaCl, CaCl₂, MgSO₄, or a combination of any two or more thereof. In any embodiment herein, the ionic strength may be 0.5, 1.0, 2.0, 3.0, or any range including and/or in-between any two of these values. When the composition comprises a salt solution at an ionic strength of 0.5 to 3.0, in any such embodiment the composition may be at a pH of about 2 to about 11 or about 11 or less; including about 3.5, about 4.0, about 4.5, about 5.0, about 5.5, about 6.0, about 6.5, about 7.0, about 7.5, about 8.0, about 8.5, about 9.0, about 9.5, about 10.0, about 10.5, about 11.0, or any range including and/or in-between any two of these values.

[0084] In another aspect, the present technology provides a method of making a functionalized colloidal silica (for example, a method of making a composition of any embodiment herein). The method includes contacting a colloidal silica with a silane according to at least one structural unit according to Formula VI, at least one structural unit according to Formula VII, at least one structural unit according to Formula VIII, or at least one structural unit according to Formula IX to yield the functionalized colloidal silica



where

R^1 is $-S-(CH_2)_nR^2$ or $-NH-NH-C(O)-(CH_2)_m-C(O)NH-NH_2$ where n is 1, 2, 3, 4, 5, or 6
and m is 1, 2, 3, 4, 5, 6, 7, or 8;

R^2 is independently at each occurrence $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$,
 $-CO_2H$, or $-CO_2^-$;

$R^{2'}$ and $R^{2''}$ are each independently H, $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$, $-CO_2H$, or $-CO_2^-$;

R^7 is hydroxyl, alkoxy, or aryloxy;

R^8 is hydroxyl, alkoxy, or aryloxy;

L^1 is alkoxy or aryloxy;

Y^1 is independently at each occurrence a cation; and

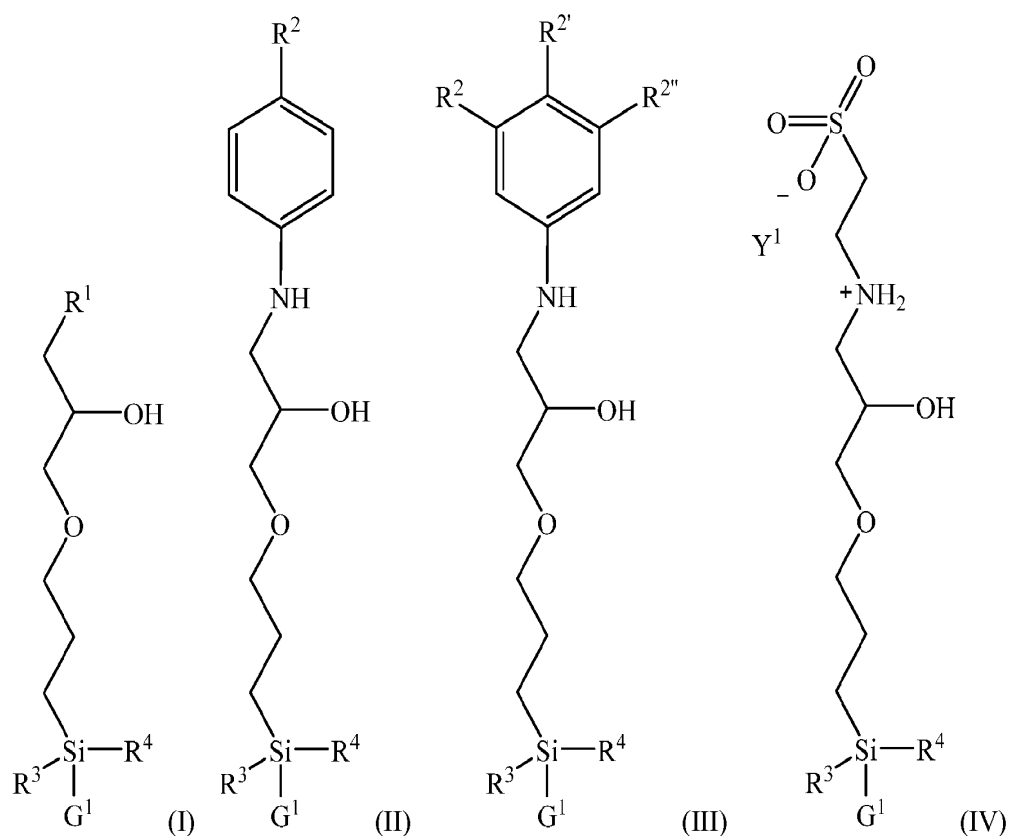
Y^2 is independently at each occurrence a cation.

[0085] The colloidal silica may be an aqueous colloidal silica.

[0086] In any embodiment herein, it may be that R^7 , R^8 , and L^1 are each independently alkoxy or aryloxy. In any embodiment herein, it may be that R^7 is hydroxyl, methoxy, ethoxy, propoxy, or phenoxy. In any embodiment herein, it may be that it may be that R^8 is hydroxyl, methoxy, ethoxy, propoxy, or phenoxy. In any embodiment herein, it may be that it may be that L^1 is methoxy, ethoxy, propoxy, or phenoxy.

[0087] In any embodiment herein of the method, it may be that the method includes a structural unit according to Formula VI and R^1 is $-(CH_2)_2SO_3Na$ and/or R^1 is $-(CH_2)_3SO_3Na$. In any embodiment herein, it may be that the method includes a structural unit according to Formula I and R^1 is $-NH-NH-C(O)-(CH_2)_4-C(O)NH-NH_2$. In any embodiment herein, it may be that the method includes a structural unit according to Formula VII and R^2 is $-SO_3Na$. In any embodiment herein, it may be that the method includes a structural unit according to Formula VIII where R^2 is $-SO_3Na$ and $R^{2'}$ and $R^{2''}$ are each independently H. In any embodiment herein, it may be that the composition includes a structural unit according to Formula VIII where R^2 is $-CO_2H$, $R^{2'}$ is H, and $R^{2''}$ is $-CO_2H$. In any embodiment herein, it may be that the composition includes a structural unit according to Formula VIII where R^2 is $-CO_2H$, $R^{2'}$ is $-CO_2H$, and $R^{2''}$ is H. In any embodiment herein, it may be that the composition includes a structural unit according to Formula VIII where R^2 is $-CO_2H$, $R^{2'}$ is $-CO_2H$, and $R^{2''}$ is $-CO_2H$. In any embodiment herein, it may be that the method includes a structural unit according to Formula IX.

[0088] In any embodiment herein of the method, the functionalized colloidal silica of the method may include a surface as well as a structural unit according to Formula I, a structural unit according to Formula II, a structural unit according to Formula III, and/or a structural unit according to Formula IV,



where

R¹ is -S-(CH₂)_nR² or -NH-NH-C(O)-(CH₂)_m-C(O)NH-NH₂ where *n* is 1, 2, 3, 4, 5, or 6 and *m* is 1, 2, 3, 4, 5, 6, 7, or 8;

R² is independently at each occurrence -SO₃Y¹, -SO₃H, -SO₃⁻, -CO₂Y², -CO₂H, or -CO₂⁻;

R^{2'} and R^{2''} are each independently H, -SO₃Y¹, -SO₃H, -SO₃⁻, -CO₂Y², -CO₂H, or -CO₂⁻;

R³ is hydroxyl, alkoxy, aryloxy, or G²;

R⁴ is hydroxyl, alkoxy, aryloxy, or G³;

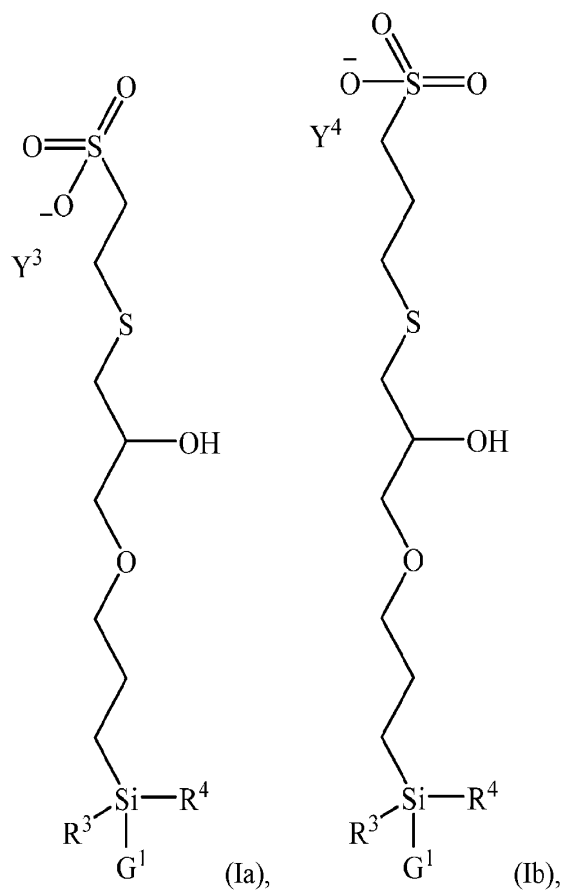
G¹, G², and G³ are each independently an oxygen atom of the surface of the silica particle, where G¹, G², and G³ are not the same oxygen atom;

Y¹ is independently at each occurrence a cation; and

Y² is independently at each occurrence a cation.

In any embodiment herein of the method, it may be that the method includes a structural unit according to Formula VI and R¹ is -(CH₂)₂SO₃Na and/or R¹ is -(CH₂)₃SO₃Na. In any

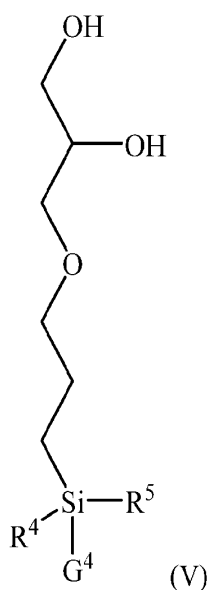
embodiment herein, it may be that the method includes a structural unit according to Formula I and R^1 is $-\text{NH}-\text{NH}-\text{C}(\text{O})-(\text{CH}_2)_4-\text{C}(\text{O})\text{NH}-\text{NH}_2$. In any embodiment herein, it may be that the method includes a structural unit according to Formula II and R^2 is $-\text{SO}_3\text{Na}$. In any embodiment herein, it may be that the method includes a structural unit according to Formula III where R^2 is $-\text{SO}_3\text{Na}$ and $R^{2'}$ and $R^{2''}$ are each independently H. In any embodiment herein, it may be that the composition includes a structural unit according to Formula III where R^2 is $-\text{CO}_2\text{H}$, $R^{2'}$ is H, and $R^{2''}$ is $-\text{CO}_2\text{H}$. In any embodiment herein, it may be that the composition includes a structural unit according to Formula III where R^2 is $-\text{CO}_2\text{H}$, $R^{2'}$ is $-\text{CO}_2\text{H}$, and $R^{2''}$ is H. In any embodiment herein, it may be that the composition includes a structural unit according to Formula III where R^2 is $-\text{CO}_2\text{H}$, $R^{2'}$ is $-\text{CO}_2\text{H}$, and $R^{2''}$ is $-\text{CO}_2\text{H}$. In any embodiment herein, it may be that the method includes a structural unit according to Formula IV. In any embodiment herein, it may be that R^3 is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G^2 . In any embodiment herein, it may be that R^4 is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G^3 . In any embodiment herein, it may be that R^3 is G^2 . In any embodiment herein, it may be that R^4 is hydroxyl. In any embodiment herein of the method, the functionalized colloidal silica may include at least one structural unit according to Formula Ia or Ib



where Y^3 and Y^4 are independently at each occurrence a cation.

[0089] In any embodiment herein of the method, Y^1 , Y^2 , Y^3 , and Y^4 may independently at each occurrence be, for example, NH_4^+ , Na^+ , Li^+ , K^+ , Ag^+ , Ca^{2+} , Mg^{2+} , or Zn^{2+} .

[0090] In any embodiment herein of the method, it may be that the functionalized colloidal silica further includes at least one structural unit according to Formula V



wherein

R⁴ is hydroxyl, alkoxy, aryloxy, or G⁵;

R⁵ is hydroxyl, alkoxy, aryloxy, or G⁶;

G^4 , G^5 , and G^6 are each independently an oxygen atom of the surface of the silica particle, where G^4 , G^5 , and G^6 are not the same oxygen atom.

[0091] In any embodiment herein of the method, it may be that R⁴ is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G⁵. In any embodiment herein of the method, it may be that it may be that R⁵ is hydroxyl, methoxy, ethoxy, propoxy, phenoxy, or G⁶.

[0092] The method of any embodiment herein may include contacting the colloidal silica with the silane in a medium, where the medium includes water and/or a polar organic solvent (*e.g.*, a polar organic solvent miscible with water). In any embodiment where the medium includes a polar organic solvent, the polar organic solvent may include methanol, ethanol, propanol, ethylene glycol, acetone, tetrahydrofuran, 1,4-dioxane, dimethylformamide, N-methylpyrrolidone, or a combination of any two or more thereof.

[0093] The method of any embodiment herein may include contacting about 1.5 to about 3.0 molecules silane per 1 nm² colloidal silica surface area. Thus, in any embodiment herein the method may include contacting an amount of molecules silane per 1 nm² colloidal silica surface

area of about 1.5, about 1.6, about 1.7, about 1.8, about 1.9, about 2.0, about 2.1, about 2.2, about 2.3, about 2.4, about 2.5, about 2.6, about 2.7, about 2.8, about 2.9, about 3.0, or any range including and/or in-between any two of these values.

[0094] The method of any embodiment herein may provide a composition comprising water and the functionalized colloidal silica (*e.g.*, of any embodiment of the composition aspect of the present technology). In such embodiments, the composition may be stable to aging for 24 hours or longer at temperature of 80 °C when the composition comprises a salt solution at an ionic strength of 0.5 to 3.0. The salt solution of any embodiment herein may include NaCl, CaCl₂, MgSO₄, or a combination of any two or more thereof. In any embodiment herein, the ionic strength may be 0.5, 1.0, 2.0, 3.0, or any range including and/or in-between any two of these values. When the composition comprises a salt solution at an ionic strength of 0.5 to 3.0, in any such embodiment the composition may be at a pH of about 2 to about 11 or about 3.5 to about 11; including about 3.5, about 4.0, about 4.5, about 5.0, about 5.5, about 6.0, about 6.5, about 7.0, about 7.5, about 8.0, about 8.5, about 9.0, about 9.5, about 10.0, about 10.5, about 11.0, or any range including and/or in-between any two of these values.

[0095] The method of any embodiment herein may include contacting a colloidal silica with a silane according to Formula V to yield an initial mixture, the initial mixture including the functionalized colloidal silica as well as unreacted silane, a silane not bonded to the colloidal silica, an impurity, or a combination of any two or more thereof; and purifying the functionalized colloidal silica by ultrafiltration of the initial mixture to separate the functionalized colloidal silica from the unreacted silane, the silane not bonded to the colloidal silica, impurity, or a combination of any two or more thereof.

[0096] In a further aspect, the present technology provides a functionalized silica prepared according to a method of any embodiment described herein.

[0097] The present technology, thus generally described, will be understood more readily by reference to the following examples, which are provided by way of illustration and are not intended to be limiting of the present technology.

EXAMPLES

[0098] Commercially available LUDOX colloidal silica grades were used in these examples. These products were supplied by W.R. Grace & Co. Similar products, such as Levasil, available from Nouryon, AMSol, available from Applied Material Solutions, Köstrosol 1540 from CWK Chemiewerk Bad Köstritz GmbH, Nalco 1140 from Nalco Water, Snowtex from Nissan Chemical, etc. can also be used.

[0099] All the chemicals used in these examples came from common suppliers such as SigmaAldrich, Fisher Scientific, TCI America and Gelest, Inc. These chemicals were purchased and used without further purifications.

[0100] To calculate the silane treatment levels for colloidal silica particles, 345 m²/g surface area was used for 7 nm grade of colloidal silica (e.g. LUDOX SM), 220 m²/g surface area for 12 nm grade of colloidal silica (e.g. LUDOX HS-40 or LUDOX AM or LUDOX CL), 140 m²/g surface area for 22 nm grade of colloidal silica (e.g. LUDOX TM-40), and 75 m²/g surface area for 40 nm grade (e.g. LUDOX PW-50 (X), a colloidal silica grade with polydispersed, different sized silica particles). The treatment level (TL) is defined as number of molecules (NM) per square nanometer of solid particle surface area, or NM/nm².

[0101] Procedures for purifying functionalized colloidal silica included using Spectrum MidiKros hollow fiber membranes (e.g. D02-E050-10-S mPES/50 kD molecular weight cut-off (MWCO) with surface area of 75 cm²) (other types of membranes with suitable molecular weight cutoff can also be used). The colloidal silica samples were passed through the membranes via Tygon tubing with a peristaltic pump under a pressure of less than 25 psi. The permeates, containing impurities such as salts, and unbonded, free organic molecules, were collected and the total volume was measured. The typical solids for the colloidal silica were between 5-25%, and fresh deionized (DI) water was added to make up the volume lost in the permeates. Typically, 5-10 volumes of permeates were accumulated against the initial total volume of the colloidal samples before the completion of the ultrafiltration process.

[0102] The general method for elemental analysis of functionalized particles for carbon (C%), hydrogen (H%), nitrogen (N%), and sulfur (S%) included placing small amounts of the purified colloidal samples in a glass vials. The vials were dried in an oven at 90°C overnight. The dried

solids were collected, and they were subjected to elemental analysis with LECO G4 ICARUS Series 2 analyzer or PerkinElmer 2400 series.

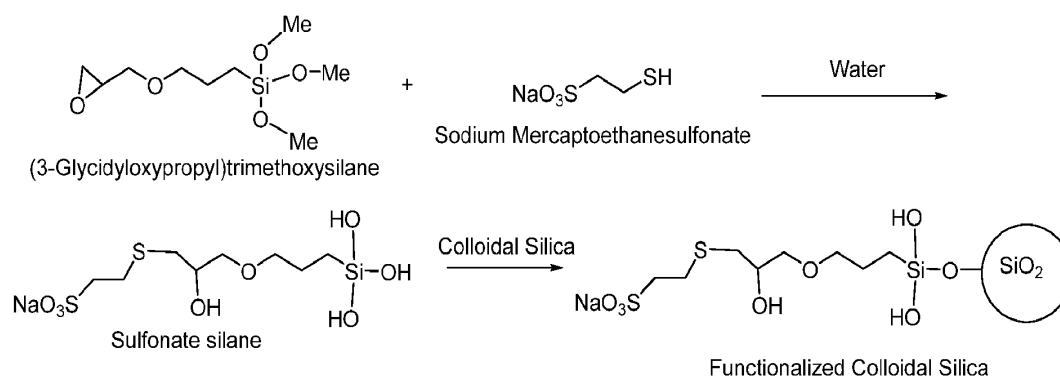
[0103] Titration methods were used. For zeta titrations, a Colloid Dynamics AcoustoSizer IIX coupled to an auto-titrator unit was used to measure zeta potentials as functions of pH by an electroacoustic method. For typical runs, colloidal solutions were prepared with 5% colloidal solids by dilution of the original sample with DI water. Potentiometric titrations were performed starting at the colloidal solutions nascent pH and run either up to pH 9 (for colloidal solutions with nascent pH less than 7) or down to pH 3 (for colloidal solutions with nascent pH greater than 7) and then back to either pH 9 or 3, respectively. The pre-loaded instrument parameters for SiO₂ (silica, amorphous-typical) and water were used by the software. Titrations were done with 0.1 N HCl and 0.1 N NaOH.

[0104] For dynamic light scattering (DLS) particle size measurement, a Malvern Zetasizer Nano-S90 model number ZEN1690 was utilized. Solutions of 2% wt colloidal solids were prepared by dilution of the original colloidal solutions with DI water. Once diluted, the colloidal solutions were filtered with a 0.45-micron syringe filter into the measurement cuvette. Measurements were accumulated for 60 seconds. The values reported are D50 on a volume basis.

[0105] Example 1 (Sodium Mercaptoethanesulfonate on LUDOX HS-40 at 2.0 NM/nm² TL)

[0106] Sodium 2-mercaptoethanesulfonate (98% purity, available from Aldrich), 3.61 g, was dissolved in 30 mL of DI water. The pH of the solution was around 5.3. To the stirred solution was added dropwise 5.20 g of (3-glycidyloxypropyl)trimethoxysilane (glycidylsilane). The mixture was stirred at room temperature for about 1 hour. In a 250 mL beaker, 75 g of LUDOX HS-40 (~30 g of dried SiO₂) was weighed, and then diluted with 30 mL of DI water. While mixing, the silane solution was slowly added into the colloidal silica dropwise, at room temperature. Once added, the solution was allowed to mix at room temperature for 1 hour. After 1 hour, the sample was heated at 60-70°C and the solution was allowed to mix for another 1 hour at this temperature. After the reaction, the mixture was allowed to cool down to room temperature and the sample was diafiltered with 6 volumes of DI water. A small sample was taken and dried at 90°C overnight and elemental analysis was carried out to determine the carbon content of the dried sample.

[0107] The following Reaction Scheme I shows the reaction scheme of this example.

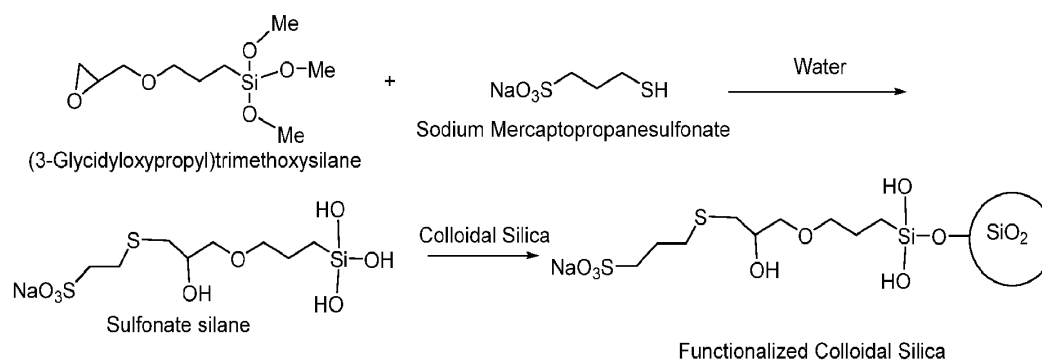


Reaction Scheme I

[0108] **Example 2** (Sodium Mercaptopropanesulfonate on LUDOX HS-40 at 2.0 NM/nm^2 TL)

[0109] Sodium 3-mercapto-1-propanesulfonate (>85% purity, available from TCI America), 4.61 g, was dissolved in 30 mL of DI water. The pH of the solution was about 1.7. To the stirred solution was added dropwise 5.20 g of (3-glycidyloxypropyl)trimethoxysilane (glycidylsilane). The mixture was stirred at room temperature for about 1 hour. In a 250 mL beaker, 75 g of LUDOX HS-40 (~30 g of dried SiO_2) was weighed and diluted with 30 mL of DI water. While mixing, the silane solution was slowly added into the colloidal silica dropwise, at room temperature. Once added, the solution was allowed to mix at room temperature for 1 hour. After 1 hour, the sample was heated at 60-70°C and allowed to mix for another 1 hour at this temperature. After the reaction, the mixture was allowed to cool down to room temperature and the sample was diafiltered with 6 volumes of DI water. A small sample was taken and dried at 90°C overnight and elemental analysis was carried out to determine the carbon content of the dried sample.

[0110] The following Reaction Scheme II shows the reaction scheme of this example.

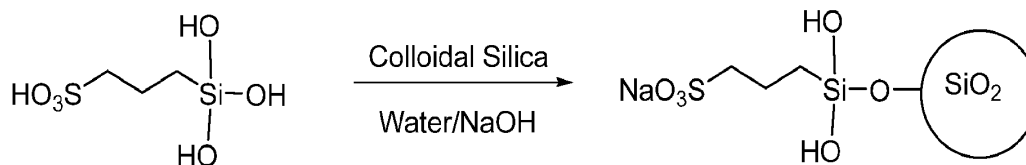


Reaction Scheme II

[0111] **Comparative Example 1** (Commercial 3-(trihydroxysilyl)-1-propanesulfonic acid on LUDOX HS-40 at 2.0 NM/nm^2 TL)

[0112] In a 250 mL beaker was added 75 g of LUDOX HS-40, diluted with 30 g of DI water. To the stirred colloidal silica, was added dropwise 12.71 g of commercial 3-(trihydroxysilyl)-1-propanesulfonic acid (30-35% concentration, available from Gelest, Inc.). During the addition, when the pH dropped to around 6.0, 1 M NaOH was added to bring the pH back to 8.0, and then the addition of silane solution was continued. This process was repeated until all the silane was added, and the final pH of the mixture was around 7.5. Once added, the solution was allowed to mix at room temperature for 1 hour. After 1 hour, the sample was heated at 60-70°C and allowed to mix for another 1 hour at this elevated temperature. After the reaction, the mixture was allowed to cool down to room temperature and the sample was diafiltered with 6 volumes of DI water. A small sample was taken and dried at 90°C overnight and elemental analysis was carried out to determine the carbon content of the dried sample.

[0113] The following Reaction Scheme III shows the reaction scheme for this Comparative Example 1.



Reaction Scheme III

[0114] Table 1 shows the carbon and sulfur contents of the corresponding dried samples in Examples 1 and 2 and Comparative Example 1.

Table 1

Example Number	Surface Group Type	C% (Based on Dried Samples)	S% (Based on Dried Samples)	Calculated SO ₃ Na (mmol/g of Dried Samples)
Example 1	Mercaptoethanesulfonate	2.76	1.37 (2 S per molecule)	0.21
Example 2	Mercaptopropanesulfonate	3.79	1.97 (2 S per molecule)	0.31
Comparative Example 1	Commercial Propanesulfonate	1.20	0.55 (1 S per molecule)	0.17

[0115] As shown, at the same treatment level, samples in Examples 1 and 2 had higher amounts of carbon and sulfur, but the calculated SO₃Na group, based on S contents, was relatively close for the three samples in these examples.

[0116] FIG. 1 is a graph of pH vs. zeta potential of colloidal silica samples modified with one of the three sulfonate groups from Example 1, Example 2, or Comparative Example 1, and unmodified HS-40. As shown in FIG. 1, when compared to unmodified HS-40, which showed typical ionization of the surface silanol groups with regards to the solution pHs, all three sulfonate functionalized modified colloidal samples showed negative zeta potential in the whole pH titration range, with little change to surface charge.

[0117] Salt Stability Test of Examples 1-2, Comparative Example and HS-40 Starting Material

[0118] Colloidal systems consisting of charged nanoparticles, stabilized by electrostatic repulsion forces, may be sensitive to high ionic strength or high concentration salt solutions, due to significantly reduced Debye length in high salt environment. For example, a solution of NaCl in water at 25°C and a concentration of 1×10^{-3} M has a Debye length of $\lambda_D = 9.6$ nm, corresponding to roughly 40 water diameters; whereas at a concentration of 0.1 M the Debye length is $\lambda_D = 0.96$ nm, equivalent to just four water diameters. Smith, Lee, and Perkin, “The electrostatic screening length in concentrated electrolytes increases with concentration.” J. Phys. Chem. Lett. 2016, 7, 12, 2157–2163. While not being bound by any theory, bonded surface organic groups on the colloidal particles may introduce steric effect and help the salt tolerance of the colloidal systems comprising the functionalized colloidal nanoparticles. Here, the colloidal stability with selected functions from the described examples was compared against the starting material as well as the samples from the comparative examples.

[0119] To standardize the salt concentrations in the stability test, sodium chloride at 2 different concentrations (1 M and 2 M) was used for salt compatibility testing of these samples.

[0120] Table 2 lists the salt stability test results. The tests were carried out at pH 7-10 (natural pH of these samples), and at pH 3, at 2% colloidal silica concentrations, and at an elevated temperature. Thus, equal volumes of the salt solutions in the Table 2 ($2 \times$ concentrations in Table 2) and 4% colloidal samples were mixed, and their colloidal stability was visually observed for 4 hours and 24 hours at 80°C. Arrhenius chemical reaction kinetics suggested that higher temperatures speed up reactions, often doubling the rate for every 10-degree rise. Thus, 24 hours at 80°C (6×10 degrees) are approximately $24 \times 2^6 = 1536$ hours (or 64 days) at 20°C (room temperature). Colloidal stability is defined as stable, turbid (less stable) or gelled (not stable) after the aging at this high temperature. The term “stable” means no visual or physical changes was observed in the colloidal dispersion after aging. The term “turbid” means that the colloidal dispersion became more whitish in color and less transparent but with no visible settlement or viscosity increase observed in the samples. The term “gelled” means that the viscosity of the colloidal dispersion increased to the extent that the whole sample did not flow as a liquid.

Table 2

Samples	Test pH	Salt Concentrations	80°C, 24 hours
HS-40	Alkaline pH	0M NaCl	Stable
		1M NaCl	Gelled
		2M NaCl	Gelled
	pH 3	0M NaCl	Stable
		1M NaCl	Gelled
		2M NaCl	Gelled
Example 1	Alkaline pH	0M NaCl	Stable
		1M NaCl	Stable
		2M NaCl	Stable
	pH 3	0M NaCl	Stable
		1M NaCl	Stable
		2M NaCl	Stable
Example 2	Alkaline pH	0M NaCl	Stable
		1M NaCl	Stable
		2M NaCl	Stable
	pH 3	0M NaCl	Stable
		1M NaCl	Stable
		2M NaCl	Stable
Comparative Example 1	Alkaline pH	0M NaCl	Stable
		1M NaCl	Turbid
		2M NaCl	Gelled
	pH 3	0M NaCl	Stable
		1M NaCl	Turbid
		2M NaCl	Gelled

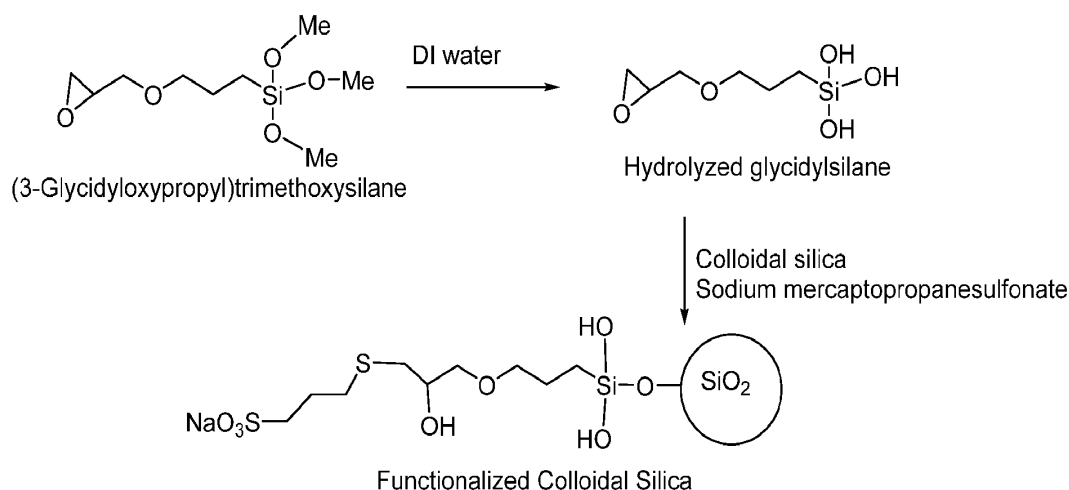
[0121] As shown in Table 2, the comparative example showed improved stability over unmodified HS-40, but both samples from Example 1 and Example 2 showed excellent stability at the two salt concentrations with no visual change after heat aging.

[0122] **Example 3** (Sodium Mercaptopropanesulfonate on LUDOX HS-40 at 1.7 NM/nm² TL, with a change of addition order)

[0123] 22.10 g of glycidylsilane was mixed with 40 mL of DI water at room temperature until a clear solution was obtained (~3 hours). In a 500 mL beaker, 150 g of LUDOX HS-40 (~60 g of dried SiO₂) was weighed and diluted with 50 mL of DI water. Sodium 3-mercpto-1-

propanesulfonate (>85% purity, available from TCI America), 18.52 g, was dissolved in 50 mL of DI water and the solution was slowly added into the stirred colloidal silica. The pH of the mixture was kept around 9.5 with diluted NaOH solution. Then, the stirred colloidal mixture was heated at 55°C with a water bath. To the stirred solution was added dropwise the glycidylsilane solution as prepared over 1 hour. After the addition, the reaction was kept at 55-60°C for another 1 hour. After the reaction, the mixture was allowed to cool down to room temperature and the sample was diafiltered with 6 volumes of DI water. A small sample was taken and dried at 90°C overnight and elemental analysis was carried out to determine the carbon content of the dried sample.

[0124] The following Reaction Scheme IV shows the reaction scheme of this Example 3.



Reaction Scheme IV

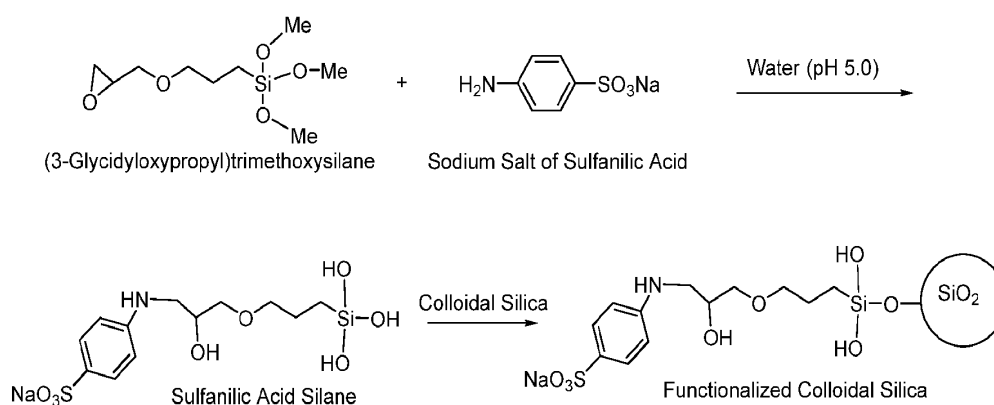
[0125] Elemental analysis of dried sample showed C% = 3.72% and S% = 0.94%. This result indicates that even though at lower treatment level (1.7 vs. 2.0 in Example 2), there was a larger drop of S% in this example, suggesting that this *in situ* process had lesser sulfonate group attachment when compared to the separate silane preparation method described in Example 2.

[0126] **Example 4** (Sulfanilic Acid Modification at 2.0 NM/nm² TL)

[0127] 11.4 g of sulfanilic acid was dissolved in 60 mL of DI water and the pH of the solution was adjusted to about 6.0 with 5 M NaOH. To the stirred solution was added 10.4 g of

glycidylsilane. The mixture was stirred at room temperature for 1 hour, and then heated at 60°C for 2 hours. In a 300 mL beaker, 150 g of LUDOX HS-40 (~60 g of dried SiO₂) were mixed with 50 mL of DI water, and to the stirred colloidal mixture was added the silane solution slowly and over 10 minutes. The resulting mixture was stirred for 1 hour at room temperature, and for 2 hours at 70°C. The sample was diafiltered with 6 volumes of DI water. Elemental analysis of a small, dried sample showed C% = 4.28%, N% = 0.40%, and S% = 0.63%. The sample was stable (no visual change) at 80°C for overnight (24 hours) at 2% solids and in 2 M NaCl at pH 9.1 as well as at pH 2.0.

[0128] The following Reaction Scheme V shows the reaction scheme of this Example 4.

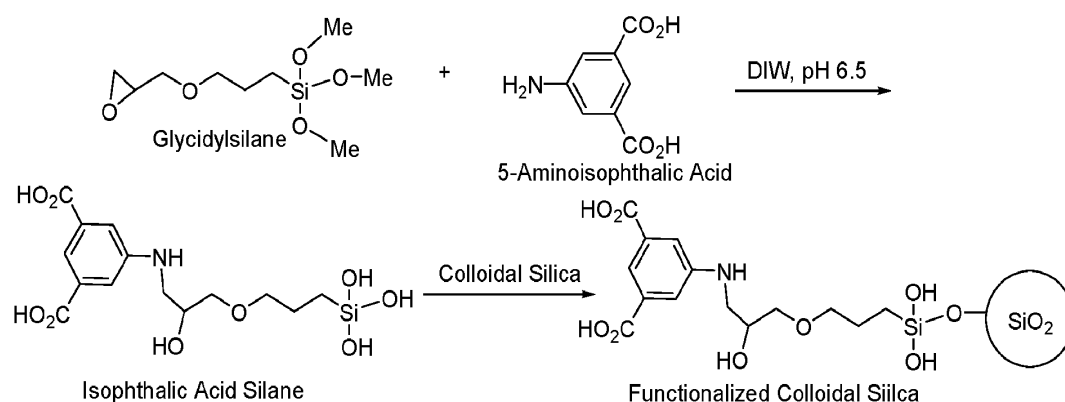


Reaction Scheme V

[0129] **Example 5** (Isophthalic Acid Modification at 1.5 NM/nm² TL)

[0130] 2.99 g of 5-aminoisophthalic acid was formed into a slurry in 80 mL of DI water. The pH of the solution was adjusted to about 6.0 with 1 M NaOH. To the stirred solution was added 3.90 g of glycidylsilane. The mixture was stirred overnight (about 15 hours) at room temperature, and the pH was kept at about 6.0 with addition of 1 M NaOH. Then the mixture was heated at 50°C until all solids were dissolved. In a 300 mL beaker, 75 g of LUDOX HS-40 (about 30 g of dried SiO₂) were mixed with 30 mL of DI water, and to the stirred colloidal mixture was added the silane solution slowly and over 10 minutes. The resulting mixture was stirred for 1 hour at room temperature, and for 2 hours at 70°C. The sample was diafiltered with 5 volumes of DI water. Elemental analysis of a small, dried sample showed C% = 3.45%, and N% = 0.22%.

[0131] The following Reaction Scheme VI shows the reaction scheme in this Example 5.



Reaction Scheme VI

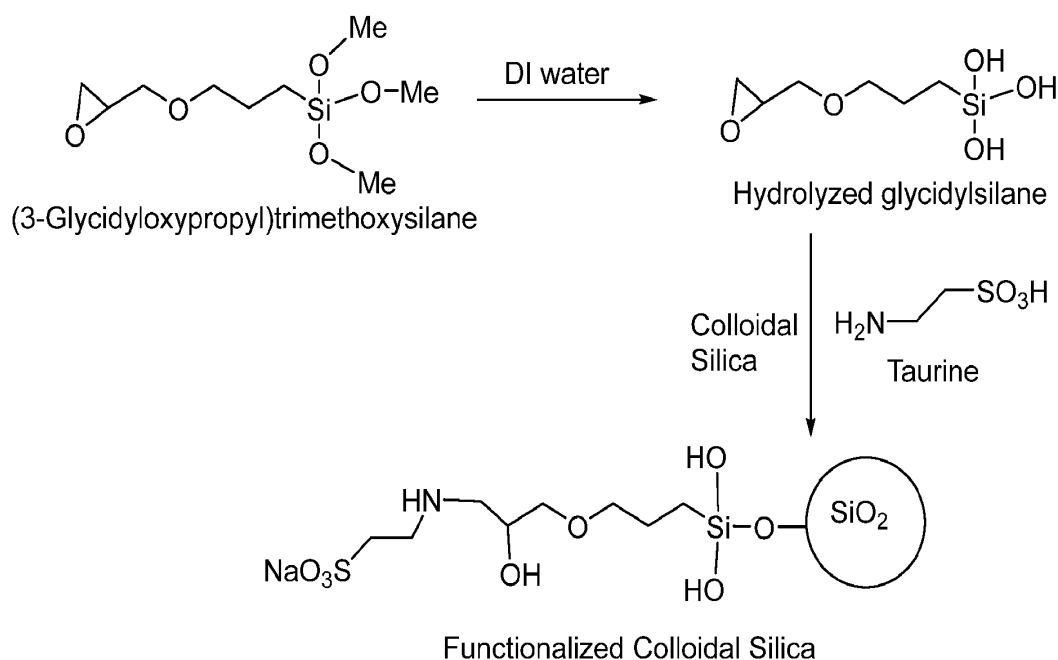
[0132] The diafiltered sample had a pH of about 10.1, and the sample was stable (no visual change) at 80°C for about 15 hours at 2% solids and in 2 M NaCl.

[0133] FIG. 2 is a graph of pH vs. zeta potential of colloidal silica samples modified according to Example 4 and Example 5, as compared to unmodified HS-40. As shown in FIG. 2, when compared to unmodified HS-40, which showed typical ionization of the surface silanol groups with pH solution, the modified samples in Examples 4 and 5 exhibited greater negative charge in the pH range of 3 to 8.

[0134] **Example 6** (Taurine Modification at 1.7 NM/nm² TL)

[0135] 81.0 g of glycidylsilane was mixed with 135 g of DI water until the silane completely dissolved (in about 2 hours). In a separate beaker, taurine, 65.0 g, was dissolved in 250 ml of DI water. The pH of the solution was adjusted to 9.5 with 1 M NaOH. In a 3 L beaker, 1375 g of LUDOX HS-40 (~550 g of dried SiO₂) were mixed with 825 ml of DI water, and to the stirred colloidal silica was added first the taurine solution, followed by the silane solution slowly. The mixture was gradually heated to 70°C and kept heated at 70°C for 2 hours. The sample was diafiltered with 5 volumes of DI water. Elemental analysis of a small, dried sample showed C% = 3.43%, and S% = 0.36%.

[0136] The following Reaction Scheme VII shows the reaction scheme of this Example 6.

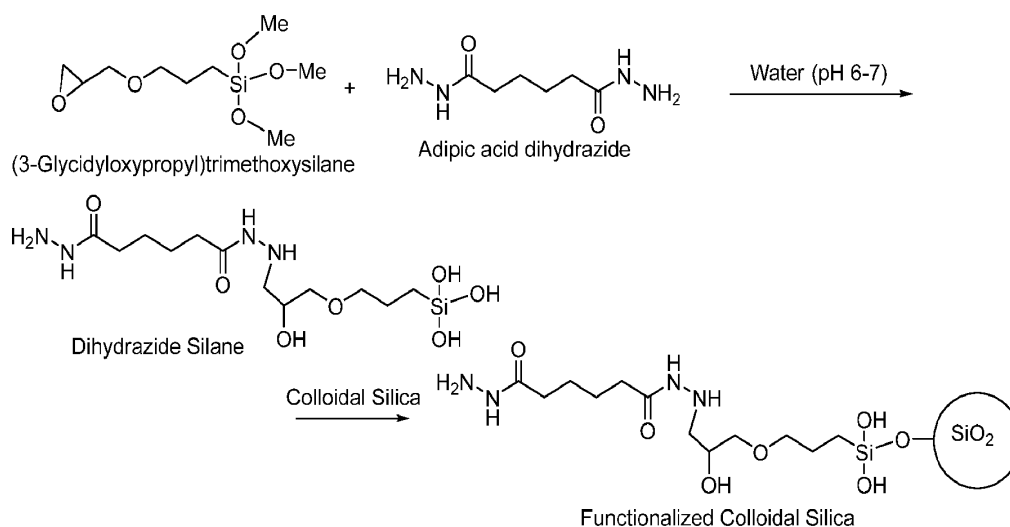


Reaction Scheme VII

[0137] **Example 7** (Hydrazide Modification)

[0138] Adipic acid dihydrazide (available from Aldrich), 122 g, was dissolved in 1 L of DI water. The solution was adjusted to around pH 6 with NaOH. To the solution, 73.7 g of glycidylsilane was added. The mixture was stirred at room temperature for 3 hours. In a separate 3 L beaker, 1250 g of LUDOX HS-40 (~500 g of dried SiO₂) were stirred. To the stirred colloidal silica was slowly added the silane solution. The mixture was gradually heated to 70°C and kept heated for 2 hours. The sample was diafiltered with 5 volumes of DI water. Elemental analysis of a small, dried sample showed C% = 5.101%, N% = 1.475%.

[0139] The following Reaction Scheme VIII shows the reaction scheme of this Example 7.



Reaction Scheme VIII

[0140] FIG. 3 is a graph of pH vs. zeta potential of the hydrazide modified colloidal silica (Example 7) as compared to unmodified HS-40.

[0141] While certain embodiments have been illustrated and described, it should be understood that changes and modifications can be made therein in accordance with ordinary skill in the art without departing from the technology in its broader aspects as defined in the following claims.

[0142] The embodiments, illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms “comprising,” “including,” “containing,” etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the claimed technology. Additionally, the phrase “consisting essentially of” will be understood to include those elements specifically recited and those additional elements that do not materially affect the basic and novel characteristics of the claimed technology. The phrase “consisting of” excludes

any element not specified. Finally, it will be understood that disclosure of one of the foregoing terms also discloses embodiments using any of the other two terms or their equivalents.

[0143] The present disclosure is not to be limited in terms of the particular embodiments described in this application. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and compositions within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions, or biological systems, which can 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.

[0144] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0145] As will be understood by one skilled in the art, for any and all purposes, particularly in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” “greater than,” “less than,” and the like, include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member.

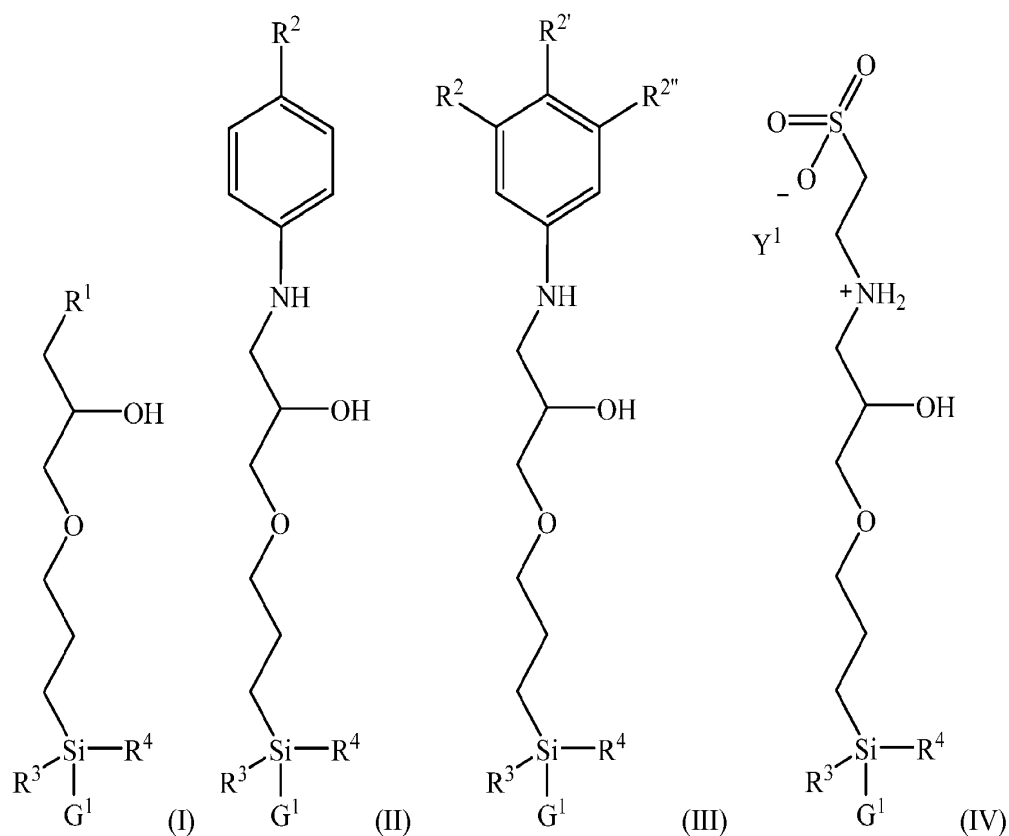
[0146] All publications, patent applications, issued patents, and other documents referred to in this specification are herein incorporated by reference as if each individual publication, patent application, issued patent, or other document was specifically and individually indicated to be

incorporated by reference in its entirety. Definitions that are contained in text incorporated by reference are excluded to the extent that they contradict definitions in this disclosure.

[0147] Other embodiments are set forth in the following claims.

WHAT IS CLAIMED IS:

1. A composition comprising water and a functionalized colloidal silica, wherein the functionalized colloidal silica comprises
- silica particles comprising a surface, and
- a structural unit according to Formula I, a structural unit according to Formula II, a structural unit according to Formula III, or a structural unit according to Formula IV



wherein

R^1 is $-S-(CH_2)_nR^2$ or $-NH-NH-C(O)-(CH_2)_m-C(O)NH-NH_2$ where n is 1, 2, 3, 4, 5, or 6 and m is 1, 2, 3, 4, 5, 6, 7, or 8;

R^2 is independently at each occurrence $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$, $-CO_2H$, or $-CO_2^-$;

$R^{2'}$ and $R^{2''}$ are each independently H, $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$, $-CO_2H$, or $-CO_2^-$;

R^3 is hydroxyl, alkoxy, aryloxy, or G^2 ;

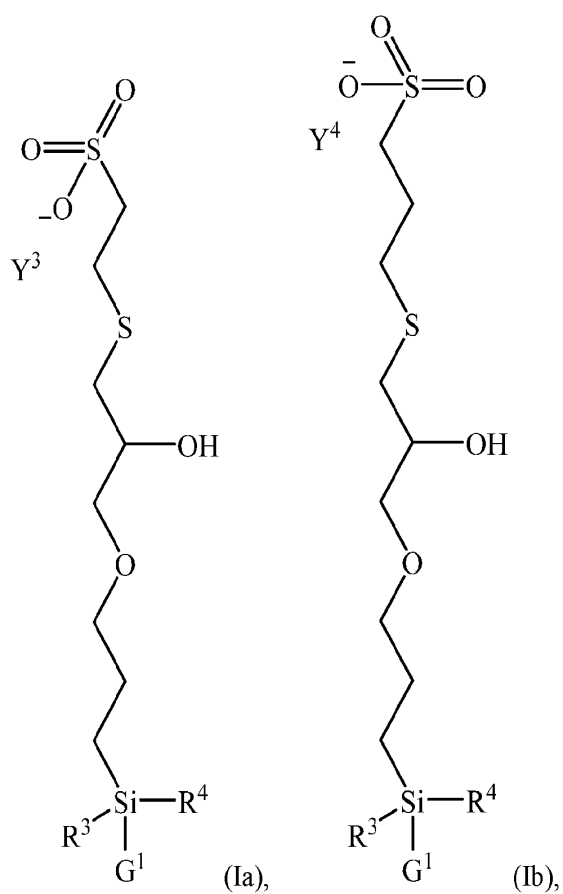
R^4 is hydroxyl, alkoxy, aryloxy, or G^3 ;

G^1 , G^2 , and G^3 are each independently an oxygen atom of the surface of the silica particle, where G^1 , G^2 , and G^3 are not the same oxygen atom;

Y^1 is independently at each occurrence a cation; and

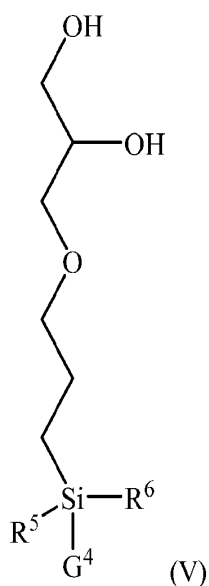
Y^2 is independently at each occurrence a cation.

2. The composition of claim 1, wherein the composition comprises a pH of about 10.5 or lower and the functionalized colloidal silica has a negative surface charge.
3. The composition of claim 2, wherein the functionalized colloidal silica comprises the structural unit according to Formula I, R^1 is $-S-(CH_2)_nR^2$, and n is 2 or 3.
4. The composition of any one of claims 1-3, wherein a median diameter of the silica particles as determined by dynamic light scattering or disc centrifuge analysis is about 1 nm to about 100 nm.
5. The composition of any one of claims 1-4, wherein the silica particles have a Sears surface area of about 25 m²/g to about 1,200 m²/g.
6. The composition of any one of claims 1-5, wherein the number of structural units according to Formula I, structural units according to Formula II, structural units according to Formula III, and structural units according to Formula IV per nm² surface area is about 0.8 to about 3.5.
7. The composition of any one of claims 1-6, wherein R^1 is $-(CH_2)_2SO_3Na$.
8. The composition of any one of claims 1-7, wherein R^3 is G^2 .
9. The composition of any one of claims 1-8, wherein R^4 is hydroxyl.
10. The composition of any one of claims 1-9, wherein the silica particles comprise at least one structural unit according to Formula Ia or Ib



where Y³ and Y⁴ are independently at each occurrence a cation.

11. The composition of any one of claims 1-10, wherein the silica particles further comprise at least one structural unit according to Formula V



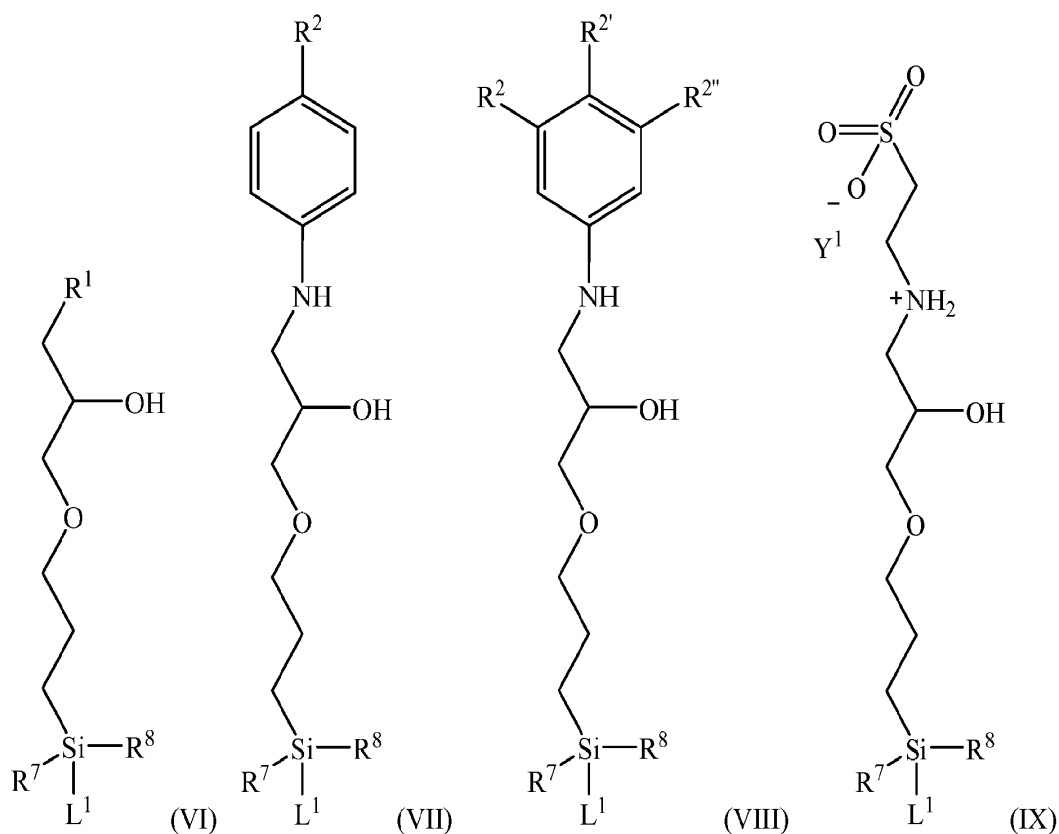
wherein

R^5 is hydroxyl, alkoxy, aryloxy, or G^5 ;

R^6 is hydroxyl, alkoxy, aryloxy, or G^6 ;

G^4 , G^5 , and G^6 are each independently an oxygen atom of the surface of the silica particle, where G^4 , G^5 , and G^6 are not the same oxygen atom.

12. The composition of any one of claims 1-11, wherein the composition comprises about 0.1 wt% to about 50 wt% of the functionalized colloidal silica.
13. The composition of any one of claims 1-12, wherein the composition is stable to aging for 24 hours or longer at temperature of 80 °C when the composition comprises a salt solution at an ionic strength of 0.5 M to 3.0 M.
14. A method of making a functionalized colloidal silica, the method comprising contacting a colloidal silica with a silane according to Formula VI, a silane according to Formula VII, a silane according to Formula VIII, or a silane according to Formula IX to yield the functionalized colloidal silica



wherein

R^1 is $-S-(CH_2)_nR^2$ or $-NH-NH-C(O)-(CH_2)_m-C(O)NH-NH_2$ where n is 1, 2, 3, 4, 5, or 6 and m is 1, 2, 3, 4, 5, 6, 7, or 8;

R^2 is independently at each occurrence $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$, $-CO_2H$, or $-CO_2^-$;

$R^{2'}$ and $R^{2''}$ are each independently H, $-SO_3Y^1$, $-SO_3H$, $-SO_3^-$, $-CO_2Y^2$, $-CO_2H$, or $-CO_2^-$;

R^7 is hydroxyl, alkoxy, or aryloxy;

R^8 is hydroxyl, alkoxy, or aryloxy;

L^1 is alkoxy or aryloxy;

Y^1 is independently at each occurrence a cation; and

Y^2 is independently at each occurrence a cation.

15. The method of claim 14, wherein R^7 , R^8 , and L^1 are each independently alkoxy or aryloxy.

16. The method of claim 14 or claim 15, wherein R^7 , R^8 , and L^1 are each independently alkoxy.

17. The method of any one of claims 14-16, wherein R^2 is $-SO_3H$ or $-SO_3^-$ and $R^{2'}$ and $R^{2''}$ are each independently H.
18. The method of any one of claims 14-17, wherein the method comprises contacting the colloidal silica with the silane in a medium comprising water.
19. The method of claim 18, wherein the method comprises contacting the colloidal silica with the silane according to Formula VI or the silane according to Formula VII, and the medium has a pH of about 4 to about 6.
20. The method of claim 18, wherein the method comprises contacting the colloidal silica with the silane according to Formula VIII, and the medium has a pH of about 2 to about 11.
21. The method of any one of claims 14-20, wherein the method comprises contacting about 1.5 to about 3.0 molecules silane per 1 nm^2 colloidal silica surface area.
22. The method of any one of claims 14-21, wherein the method provides a composition according to any one of claims 1-13.
23. A functionalized silica prepared according to a method of any one of claims 14-22.
24. A formulation for use in enhanced oil recovery, metal surface treatment, electroplating, coating, and/or paint, wherein the formulation comprises a composition according to any one of claims 1-13.
25. A formulation for use in enhanced oil recovery, metal surface treatment, electroplating, coating, and/or paint, wherein the formulation comprises a functionalized silica prepared according to a method of any one of claims 14-22.