



(51) International Patent Classification:

H01F 1/00 (2006.01) *H01F 1/053* (2006.01)
H01F 7/02 (2006.01) *H01F 41/00* (2006.01)
H01F 1/06 (2006.01) *B82Y 5/00* (2011.01)

(21) International Application Number:

PCT/US2016/021024

(22) International Filing Date:

4 March 2016 (04.03.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/129,551 6 March 2015 (06.03.2015) u s

(71) Applicant: **SDCMATERIALS, INC.** [US/US]; 940 S. Park Lane, Suite 2, Tempe, AZ 85281 (US).

(72) Inventors: **BIBERGER, Maximilian, A.**; C/o Sdcmaterials, Inc., 940 S. Park Lane, Suite 2, Tempe, AZ 85281 (US). **KEARL, Bryant**; C/o Sdcmaterials, Inc., 940 S. Park Lane, Suite 2, Tempe, AZ 85281 (US). **LEAMON, David**; C/o Sdcmaterials, Inc., 940 S. Park Lane, Suite 2, Tempe, AZ 85281 (US).

(74) Agents: **CERPA, Robert K.** et al; Morrison & Foerster LLP, 755 Page Mill Road, Palo Alto, CA 94304-1018 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*):

AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*):

ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: COATED MAGNETIC PARTICLE AND METHODS OF MAKING AND USING THE SAME

(57) Abstract: The present disclosure relates to nano-sized magnetic particles, such as neodymium-iron-boron rare earth magnetic particles, and encapsulated magnetic nanoparticles, which include a magnetic nanoparticle core encapsulated by a protective layer. Magnetic nanoparticles can be encapsulated in, for example, a silane-derivative protective layer or a phosphate-containing protective layer. Also provided are nanocomposite permanent magnets comprising magnetic nanoparticles and encapsulated magnetic nanoparticles. Further provided are methods of making and using the same.



WO 2016/144811 A1

COATED MAGNETIC PARTICLES AND METHODS OF MAKING AND USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims priority benefit of United States Provisional Patent Application No. 62/129,551, filed March 6, 2015. The entire contents of that application are hereby incorporated by reference herein.

FIELD OF THE INVENTION

10 [0002] The present invention relates to the field of magnets and magnetic particles. More specifically, the present invention relates to encapsulated magnetic nanoparticles, composite magnets, and methods of making and using the same.

BACKGROUND OF THE INVENTION

15 [0003] Neodymium-iron-boron ($\text{Nd}_2\text{Fe}_{14}\text{B}$) magnets are among the most commonly used permanent magnets for industrial purposes because they are lightweight and exhibit a strong magnetic field. These magnets are generally made from a neodymium, iron, and boron materials melted, mixed, and cooled to form alloy magnetic ingots. The alloy is then be ground into micron-sized powder, pressed, and sintered to form a desired shape magnet. To form larger-
20 structured magnets, the magnetization of the micron-sized particles is generally aligned by applying an external magnetic field while bonding the particles together, resulting in a composite magnet used in a variety of applications.

[0004] Despite the strength of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets formed from micron-sized particle composites, developing technologies increasingly demand even stronger and more stable
25 permanent magnets. $\text{Nd}_2\text{Fe}_{14}\text{B}$ forms a tetragonal crystalline structure displaying high uniaxial magnetocrystalline anisotropy, allowing the material to exhibit a strong coercive field. However, micron-sized particles generally contain several unaligned $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystals. The polycrystalline microstructure of the micron-sized particle results in a weakened magnetic field. Further, the relatively large size of the micron-sized particle increases the difficulty of aligning
30 the individual magnetic domains when forming a composite magnet.

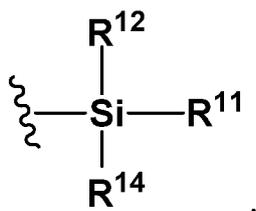
[0005] One theoretical high-strength magnet, frequently termed an exchange spring magnet, exploits the strong coercive properties of Nd₂Fe₁₄B materials (hard phase magnets) by mixing Nd₂Fe₁₄B particles with other magnetic materials demonstrating a high magnetic saturation but low coercivity (soft phase magnets). A composite including both hard and soft magnetic components should demonstrate a large magnetic energy product if the materials are of small enough scale. Jones discusses certain of these magnetic materials in Nature 472:22-23.

SUMMARY OF THE INVENTION

[0006] The disclosure herein relates to encapsulated magnetic nanoparticles, permanent magnets made from the encapsulated magnetic nanoparticles, and methods of making and using these encapsulated magnetic nanoparticles and permanent magnets.

[0007] The encapsulated magnetic nanoparticles disclosed herein comprise a magnetic nanoparticle core encapsulated by a protective layer, such as a silane-derivative protective layer or a phosphate-containing protective layer. In some embodiments, the magnetic nanoparticle core is a metallic magnetic nanoparticle core, such as a magnetic metal, magnetic alloy, or magnetic metal alloy. In some embodiments, the magnetic nanoparticle core is a rare-earth magnetic nanoparticle core. In some embodiments, the magnetic nanoparticle core is not a rare-earth magnetic nanoparticle core. In some embodiments, the magnetic nanoparticle core comprises neodymium, iron, boron, carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium. In some embodiments, the magnetic nanoparticle core comprises neodymium, iron, and boron. In some embodiments, the magnetic nanoparticle core is plasma generated. In some embodiments, the magnetic nanoparticle core is not produced by ball milling. In some embodiments, the magnetic nanoparticle core has a diameter of about 0.5 nm to about 100 nm, for example of about 1 nm to about 10 nm, or of about 3 nm to about 5 nm.

[0008] In some embodiments, the magnetic nanoparticle core is encapsulated by a protective layer, such as a silane derivative, for example a hydrophobic silane derivative. In some embodiments, the silane derivative has the formula



wherein R¹¹ is a hydrophobic group; and R¹² and R¹⁴ are independently selected from the group consisting of -Ci-C₄ alkyl, -OCi-C₄ alkyl, halo, chloro, bromo, and iodo. In some embodiments, R¹¹ is C₂-Ci₈ alkyl or C₃-Ci₈ n-alkyl. In some embodiments, R¹¹ is selected from C₆-Ci₈ alkyl. In some embodiments, R¹² and R¹⁴ are independently selected from the group consisting
5 of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro. In some embodiments, silane derivative is dimethyl octylsilane or chloromethyl octylsilane.

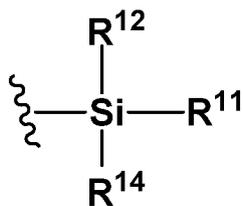
[0009] In some embodiments, the magnetic nanoparticle core is encapsulated by a phosphate-containing protective layer. In some embodiments, the protective layer is about 5 nm thick or less, about 2 nm thick or less, or about 1 nm thick or less.

10 [0010] Also described herein are permanent magnets. In some embodiments, a permanent magnet comprises a material, the material comprising a plurality of the encapsulated magnetic nanoparticles described herein. In some embodiments, the material further comprises a plurality of micron-sized particles. In some embodiments, the micron-sized particles comprise magnetic micron-sized particles. In some embodiments, the micron-sized particles comprise encapsulated
15 micron-sized particles. In some embodiments, the micron-sized particles comprise unencapsulated micron-sized particles. In some embodiments, the material is bonded together. In some embodiments, the material is cold pressed together. In some embodiments, an external magnetic field is applied to the material while the material is bonded or cold pressed together. In some embodiments, the material is sintered together. In some embodiments, the material is
20 sintered together using spark-plasma sintering. In some embodiments, the material comprises a soft magnet component. In some embodiments, the permanent magnet are molded or machined into a desired shape. The permanent magnets described herein can be used for any purpose, for example in some embodiments a permanent magnet is used in a motor or generator.

[0011] In some embodiments, a permanent magnet comprises a material, the material
25 comprising a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer or a residue thereof. In some embodiments, the material further comprises a plurality of micron-sized particles. In some embodiments, the micron-sized particles comprise magnetic micron-sized particles. In some embodiments, the micron-sized particles comprise encapsulated micron-sized
30 particles. In some embodiments, the micron-sized particles comprise unencapsulated micron-sized particles. In some embodiments, the protective layer comprises a silane-derivative. In

some embodiments, the protective layer comprises phosphate. In some embodiments, the magnetic nanoparticle cores are metallic magnetic nanoparticle cores. In some embodiments, the magnetic nanoparticle cores are rare-earth magnetic nanoparticle cores. In some embodiments, the magnetic nanoparticle cores are not rare-earth magnetic nanoparticle cores. In some
 5 embodiments, the magnetic nanoparticle cores comprise neodymium, iron, and boron. In some embodiments, the magnetic nanoparticle cores comprise carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium. In some embodiments, the magnetic nanoparticle cores are plasma generated. In some embodiments, the magnetic nanoparticle cores are not produced by ball milling. In some embodiments, 80% or more of the magnetic cores of the plurality of
 10 encapsulated magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm, or about 3 nm to about 5 nm.

[0012] In some embodiments of the permanent magnet, the silane derivative is a hydrophobic silane derivative. In some embodiments, the silane derivative has the formula



15 wherein R¹¹ is a hydrophobic group; and R¹² and R¹⁴ are independently selected from the group consisting of -Ci-C₄ alkyl, -OCi-C₄ alkyl, halo, chloro, bromo, and iodo. In some embodiments, R¹¹ is C₂-Ci₈ alkyl or C₃-Ci₈ n-alkyl. In some embodiments, R¹¹ is selected from C₆-Ci₈ alkyl. In some embodiments, R¹² and R¹⁴ are independently selected from the group consisting
 20 of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro. In some embodiments, silane derivative is dimethyl octylsilane or chloromethyl octylsilane.

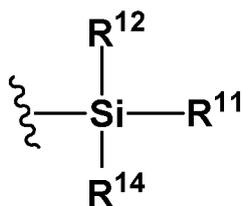
[0013] In some embodiments of the permanent magnet, the protective layer or residue thereof is about 5 nm thick or less, about 2 nm thick or less, or about 1 nm thick or less. In some embodiments, the permanent magnet is molded or machined into a desired shape. In some embodiments, the permanent magnet is used in a generator, turbine, or motor.

25 [0014] Further disclosed herein is a permanent magnet formed by bonding together a material, the material comprising a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer. In some embodiments, the material further comprises a plurality of micron-sized particles.

In some embodiments, the micron-sized particles comprise magnetic micron-sized particles. In some embodiments, the micron-sized particles comprise encapsulated micron-sized particles. In some embodiments, the micron-sized particles comprise unencapsulated micron-sized particles. In some embodiments, the protective layer comprises a silane-derivative. In some embodiments, the protective layer comprises phosphate. In some embodiments, the material is cold pressed together. In some embodiments, an external magnetic field is applied to the material while the material is bonded or cold pressed together. In some embodiments, the material is sintered together. In some embodiments, the material is spark-plasma sintered together.

[0015] In some embodiments of permanent magnets formed by the methods disclosed herein, the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are metallic magnetic nanoparticle cores. In some embodiments of permanent magnets formed by the methods disclosed herein, the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are rare-earth magnetic nanoparticle cores. In some embodiments of permanent magnets formed by the methods disclosed herein, the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are not rare-earth magnetic nanoparticle cores. In some embodiments of permanent magnets formed by the methods disclosed herein, the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles comprise neodymium, iron, and boron. In some embodiments, the r magnetic nanoparticle cores further comprise carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium. In some embodiments, the r magnetic nanoparticle cores are plasma generated. In some embodiments, the magnetic nanoparticles are not produced by ball milling. In some embodiments, 80% or more of the magnetic cores of the plurality of encapsulated magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm, or about 3 nm to about 5 nm.

[0016] In some embodiments of the permanent magnet formed by the methods disclosed herein, the silane derivative is a hydrophobic silane derivative. In some embodiments, the silane derivative has the formula



wherein R¹¹ is a hydrophobic group; and R¹² and R¹⁴ are independently selected from the group consisting of -C_i-C₄ alkyl, -OC_i-C₄ alkyl, halo, chloro, bromo, and iodo. In some embodiments, R¹¹ is C₂-C₈ alkyl or C₃-C₈ n-alkyl. In some embodiments, R¹¹ is selected from C₆-C₈ alkyl. In some embodiments, R¹² and R¹⁴ are independently selected from the group consisting
5 of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro. In some embodiments, the silane derivative is dimethyl octylsilane or chloromethyl octylsilane.

[0017] In some embodiments of the permanent magnet formed by the methods disclosed herein, the protective layer is about 5 nm thick or less, about 2 nm thick or less, or about 1 nm thick or less.

10 [0018] In some embodiments, the permanent magnets of the permanent magnet formed by the methods disclosed herein comprise a soft magnet component. In some embodiments, the permanent magnet is molded or machined into a desired shape. In some embodiments, the permanent magnet described herein is used for any purpose, for example in some embodiments a permanent magnet is used in a motor or generator.

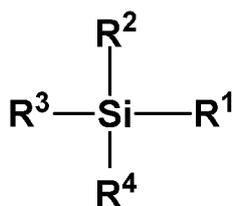
15 [0019] Further described herein are methods of making encapsulated magnetic nanoparticles comprising suspending a plurality of magnetic nanoparticles in an inert solvent to form a dispersion; combining the dispersion with sodium borohydride; and combining the dispersion with a protective-layer reagent. In some embodiments, the protective-layer reagent is a silanization reagent. In some embodiments, the protective-layer reagent is a phosphorylation
20 reagent. In some embodiments, the inert solvent is an alcohol. In some embodiments, the inert solvent is methanol or isopropanol. In some embodiments, the method of making encapsulated magnetic nanoparticles further comprises nano-sizing micron-sized magnetic particles to form the plurality of magnetic nanoparticles. In some embodiments, the nano-sizing step is performed using plasma. In some embodiments, the nano-sizing step is not performed by ball milling. In
25 some embodiments, the plurality of magnetic nanoparticles has an average diameter of about 30 nm or less, about 20 nm or less, about 10 nm or less, or about 5 nm or less. In some embodiments the encapsulated magnetic nanoparticles are washed, for example in an inert solvent. In some embodiments, 80% or more of the magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm, or about 3 nm to about 5 nm.

30 [0020] In some embodiments, the method of making encapsulated magnetic nanoparticles further comprises washing the encapsulated magnetic nanoparticles. In some embodiments, the

washing step occurs in an inert solvent. In some embodiments, the method of making encapsulated magnetic nanoparticles further comprises centrifuging the dispersion. In some embodiments, the method of making encapsulated magnetic nanoparticles further comprises soniciating the dispersion. In some embodiments, the method of making encapsulated magnetic nanoparticles further comprises combining the dispersion with sodium hydroxide. In some
 5 embodiments, the method of making encapsulated magnetic nanoparticles further comprises drying the encapsulated magnetic nanoparticles.

[0021] In some embodiments of a method making an encapsulated magnetic nanoparticle, the magnetic nanoparticles are metallic magnetic nanoparticles. In some embodiments of a method
 10 making an encapsulated magnetic nanoparticle, the magnetic nanoparticles are rare-earth magnetic nanoparticles. In some embodiments of a method making an encapsulated magnetic nanoparticle, the magnetic nanoparticles are not rare-earth magnetic nanoparticles. In some embodiments, the magnetic nanoparticles comprise neodymium, iron, and boron. In some embodiments, the magnetic nanoparticles comprise carbon, cobalt, copper, dysprosium, gallium,
 15 niobium, zinc, or zirconium.

[0022] In some embodiments of the method making an encapsulated magnetic nanoparticle, the phosphorylation reagent is phosphoric acid. In some embodiments, the silanization reagent is a hydrophobic silanization reagent. In some embodiments, the silanization reagent has the formula



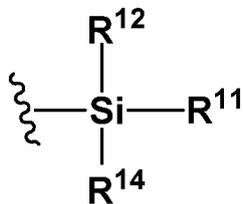
20 wherein R^1 is a hydrophobic group, and R^2 and R^4 are independently selected from the group consisting of $-\text{Ci}-\text{C}_4$ alkyl, $-\text{OCi}-\text{C}_4$ alkyl, halo, chloro, bromo, and iodo, and R^3 is a leaving group. In some embodiments, R^1 is C_2 - C_8 alkyl or C_3 - C_{18} n-alkyl. In some embodiments, R^1 is selected from C_6 - C_8 alkyl. In some embodiments, R^2 and R^4 are independently selected from
 25 the group consisting of $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, and chloro. In some embodiments, R^3 is a iodo, bromo, chloro, or sulfonate. In some embodiments, the silanization reagent is dimethylchloro octylsilane or dichloromethyl octylsilane.

[0023] Also described herein is a method of making a permanent magnet comprising bonding together a material comprising a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer. In some embodiments, the material further comprises a plurality of micron-sized particles. In some embodiments, the micron-sized particles comprise magnetic micron-sized particles. In some embodiments, the micron-sized particles comprise encapsulated micron-sized particles. In some embodiments, the micron-sized particles comprise unencapsulated micron-sized particles. In some embodiments, the method of making a permanent magnet comprises combining the plurality of micron-sized particles with the plurality of encapsulated magnetic nanoparticles. In some embodiments, the method of making a permanent magnet comprises combining a plurality of soft magnetic particles with the plurality of encapsulated magnetic nanoparticles. In some embodiments, the protective layer is a silane-derivative protective layer. In some embodiments, the protective layer is a phosphate-containing protective layer. In some embodiments, the encapsulated magnetic nanoparticles are cold pressed together.

[0024] In some embodiments, the method of making a permanent magnet comprises cold pressing the material. In some embodiments, an external magnetic field is applied during the bonding step or the cold-pressing step. In some embodiments, the method of making a permanent magnet comprises sintering the material. In some embodiments, the method of making a permanent magnet comprises spark-plasma sintering the material.

[0025] In some embodiments of a method of making a permanent magnet, the magnetic nanoparticle cores are metallic magnetic nanoparticle cores. In some embodiments of a method of making a permanent magnet, the magnetic nanoparticle cores are rare-earth magnetic nanoparticle cores. In some embodiments of a method of making a permanent magnet, the magnetic nanoparticle cores are not rare-earth magnetic nanoparticle cores. In some embodiments of a method of making a permanent magnet, the magnetic nanoparticle cores comprise neodymium, iron, and boron. In some embodiments, the magnetic nanoparticle cores comprise carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium. In some embodiments, the magnetic nanoparticle cores are plasma generated. In some embodiments, the magnetic nanoparticles are not produced by ball milling. In some embodiments, 80% or more of the magnetic nanoparticle cores have a diameter of about 0.5 nm to about 100 nm, or about 3 nm to about 5 nm.

[0026] In some embodiments of the method of making a permanent magnet, the silane derivative is a hydrophobic silane derivative. In some embodiments, the silane derivative has the formula



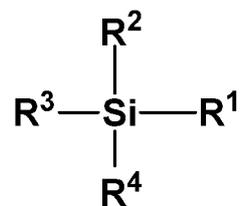
5 wherein R^{11} is a hydrophobic group; and R^{12} and R^{14} are independently selected from the group consisting of $-\text{Ci}-\text{C}_4$ alkyl, $-\text{OCi}-\text{C}_4$ alkyl, halo, chloro, bromo, and iodo. In some embodiments, R^{11} is C_2 - Ci_8 alkyl or C_3 - Ci_8 n-alkyl. In some embodiments, R^{11} is selected from C_6 - Ci_8 alkyl. In some embodiments, R^{12} and R^{14} are independently selected from the group consisting of $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, and chloro. In some embodiments, the silane derivative
10 is dimethyl octylsilane or chloromethyl octylsilane. In some embodiments the phosphate is derived from phosphoric acid. In some embodiments of a permanent magnet, the protective layer is about 5 nm thick or less, about 2 nm thick or less, or about 1 nm thick or less.

[0027] In some embodiments of the method of making a permanent magnet, the plurality of encapsulated magnetic nanoparticles is formed by suspending a plurality of magnetic
15 nanoparticles in an inert solvent to form dispersion, combining the dispersion with sodium borohydride, and combining the dispersion with a protective-layer reagent. In some embodiments, the protective-layer reagent is a silanization reagent. In some embodiments, the protective-layer reagent is a phosphorylation reagent. In some embodiments, the inert solvent is an alcohol. In some embodiments, the inert solvent is methanol or isopropanol.

20 [0028] In some embodiments of the method of making a permanent magnet, the method further comprises nano-sizing a plurality of micron-sized magnetic particles to form the plurality of magnetic nanoparticles. In some embodiments the nano-sizing step is performed using plasma. In some embodiments, the nano-sizing step is not performed by ball milling. In some embodiments, the method comprises washing the encapsulated magnetic nanoparticles. In some
25 embodiments, the washing step occurs in an inert solvent. In some embodiments, the method comprises centrifuging the dispersion. In some embodiments, the method comprises sonicating the dispersion. In some embodiments, the method comprises combining sodium hydroxide with

the dispersion. The some embodiments, the method comprises drying the encapsulated magnetic nanoparticles.

[0029] In some embodiments of the method of making a permanent magnet, the silanization reagent is a hydrophobic silanization reagent. In some embodiments, the silanization reagent has
5 the formula:



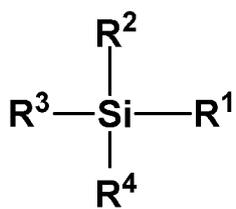
wherein R^1 is a hydrophobic group; R^2 and R^4 are independently selected from the group consisting of $-\text{Ci}-\text{C}_4$ alkyl, $-\text{OCi}-\text{C}_4$ alkyl, halo, chloro, bromo, and iodo; and R^3 is a leaving
10 group. In some embodiments, R^1 is $-\text{C}_2-\text{C}_{18}$ alkyl or $-\text{C}_3-\text{C}_{18}$ n-alkyl. In some embodiments of the method of making a permanent magnet, R^1 is selected from $-\text{C}_6-\text{C}_{18}$ alkyl. In some
embodiments, R^2 and R^4 are independently selected from the group consisting of $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, and chloro. In some embodiments, R^3 is selected from the group
consisting of iodo, bromo, chloro, or sulfonate. In some embodiments, the silane derivative is
15 dimethylchloro octylsilane or dichloromethyl octylsilane. In some embodiments, the phosphorylation reagent is phosphoric acid.

[0030] Further described herein is a method of making a permanent magnet comprising forming a material comprising a plurality of encapsulated magnetic nanoparticles, the
encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a
protective layer; and bonding the material together. In some embodiments, forming the material
20 comprises suspending a plurality of magnetic nanoparticles in an inert solvent to form a dispersion; combining the dispersion with sodium borohydride; and combining the dispersion
with a protective-layer reagent, thereby forming the plurality of encapsulated magnetic
nanoparticles.

[0031] In some embodiments, the method of making a permanent magnet further comprises
25 nano-sizing a plurality of micron-sized magnetic particles to form the plurality of magnetic
nanoparticles. In some embodiments, the nano-sizing step is performed using plasma. In some
embodiments, the nano-sizing step is not performed by ball milling. In some embodiments, the
inert solvent is an alcohol. In some embodiments, the inert solvent is methanol or isopropanol.

In some embodiments, the method comprises sonicating the dispersion. In some embodiments, the method comprises centrifuging the dispersion. In some embodiments, the method comprises combining sodium hydroxide into the dispersion.

[0032] In some embodiments of the method of making a permanent magnet described herein, the protective-layer reagent is a silanization reagent. In some embodiments, the silanization reagent is a hydrophobic silanization reagent. In some embodiments, the silanization reagent has the formula:



wherein R^1 is a hydrophobic group; R^2 and R^4 are independently selected from the group consisting of $-\text{Ci}-\text{C}_4$ alkyl, $-\text{OCi}-\text{C}_4$ alkyl, halo, chloro, bromo, and iodo; and R^3 is a leaving group. In some embodiments, R^1 is $-\text{C}_2-\text{C}_{18}$ alkyl or $-\text{C}_3-\text{C}_{18}$ n-alkyl. In some embodiments, R^1 is selected from $-\text{C}_6-\text{C}_{18}$ alkyl. In some embodiments, R^2 and R^4 are independently selected from the group consisting of $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-\text{OCH}_3$, $-\text{OCH}_2\text{CH}_3$, and chloro. In some embodiments, R^3 is selected from the group consisting of iodo, bromo, chloro, or sulfonate. In some embodiments, the silanization reagent is dimethylchloro octylsilane or dichloromethyl octylsilane. In some embodiments, the protective-layer reagent is a phosphorylation reagent. In some embodiments, the phosphorylation reagent is phosphoric acid.

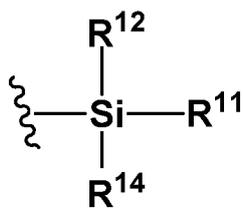
[0033] In some embodiments of the method of making a permanent magnet described herein, forming a material comprises washing the encapsulated magnetic nanoparticles. In some embodiments, the washing step occurs in an inert solvent. In some embodiments, forming a material comprises drying the encapsulated magnetic nanoparticles.

[0034] In some embodiments of the method of making a permanent magnet, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 30 nm or less. In some embodiments, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 20 nm or less. In some embodiments, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 10 nm or less. In some embodiments, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 5 nm or less. In some

embodiments, 80% or more of the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm. In some embodiments, 80% or more of the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have a diameter of about 3 nm to about 5 nm.

5 [0035] In some embodiments of the method of making a permanent magnet, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles are metallic magnetic nanoparticle cores. In some embodiments of the method of making a permanent magnet, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles are rare-earth magnetic nanoparticle cores. In some embodiments of the method of making a permanent magnet, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles are not rare-earth magnetic nanoparticle cores. In some embodiments of the method of making a permanent magnet, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise neodymium, iron, and boron. In some embodiments, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise carbon, cobalt, copper, dysprosium, gallium, 10 niobium, zinc, or zirconium. In some embodiments, the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise niobium.

[0036] In some embodiments of the method of making a permanent magnet, the protective layer comprises a silane derivative. In some embodiments, the silane derivative is a hydrophobic silane derivative. In some embodiments, the silane derivative has the formula:



20 wherein R¹¹ is a hydrophobic group; and R¹² and R¹⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo. In some embodiments, R¹¹ is -C₂-C₁₈ alkyl or -C₃-C₈ n-alkyl. In some embodiments, R¹¹ is selected from -C₆-C₁₈ alkyl. In some embodiments, R¹² and R¹⁴ are independently selected from the group consisting of - 25 CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro. In some embodiments, the silane derivative is dimethyl octylsilane or chloromethyl octylsilane. In some embodiments, the protective layer comprises phosphate. In some embodiments, the protective layer is about 5 nm thick or less, about 2 nm thick or less, or about 1 nm thick or less.

[0037] In some embodiments of the method of making a permanent magnet, forming the material further comprises combining a plurality of micron-sized particles with the plurality of encapsulated magnetic nanoparticles. In some embodiments, the micron-sized particles comprise magnetic micron-sized particles. In some embodiments, the micron-sized particles comprise 5 encapsulated micron-sized particles. In some embodiments, the micron-sized particles comprise unencapsulated micron-sized particles. In some embodiments, the method comprises cold pressing the material. In some embodiments, an external magnetic field is applied during the bonding step or cold pressing step. In some embodiments, the method comprises sintering the material. In some embodiments, the method comprises spark-plasma sintering the material. In 10 some embodiments, forming the material comprises combining a plurality of soft magnetic particles with the plurality of encapsulated magnetic nanoparticles.

[0038] Further described herein is a permanent magnet made from any of the methods of making a permanent magnet as described herein.

[0039] It is understood that aspects and embodiments of the invention described herein include 15 "consisting" and/or "consisting essentially of" aspects and embodiments. For all methods, systems, compositions, and devices described herein, the methods, systems, compositions, and devices can either comprise the listed components or steps, or can "consist of" or "consist essentially of" the listed components or steps. When a system, composition, or device is described as "consisting essentially of" the listed components, the system, composition, or 20 device contains the components listed, and may contain other components which do not substantially affect the performance of the system, composition, or device, but either do not contain any other components which substantially affect the performance of the system, composition, or device other than those components expressly listed; or do not contain a sufficient concentration or amount of the extra components to substantially affect the 25 performance of the system, composition, or device. When a method is described as "consisting essentially of" the listed steps, the method contains the steps listed, and may contain other steps that do not substantially affect the outcome of the method, but the method does not contain any other steps which substantially affect the outcome of the method other than those steps expressly listed.

[0040] Any of the embodiments described above and herein are suitable for use in permanent 30 magnets, computer hard disks, motors, turbines, or generators.

[0041] The systems, compositions, substrates, and methods described herein, including any embodiment of the invention as described herein, may be used alone or may be used in combination with other systems, compositions, substrates, and methods.

5

BRIEF DESCRIPTION OF THE FIGURE

[0042] FIG. 1 depicts one embodiment of an encapsulated magnetic nanoparticle.

DETAILED DESCRIPTION OF THE INVENTION

[0043] Magnetic nanoparticles, encapsulated magnetic nanoparticles, and methods of making of making and using such magnetic nanoparticles are provided herein. Further provided are nanocomposite permanent magnets comprising magnetic nanoparticles or encapsulated magnetic nanoparticles. The magnetic nanoparticles and encapsulated magnetic nanoparticles can be magnetic nanoparticles. Preferably, the magnetic nanoparticles and encapsulated magnetic nanoparticles are rare-earth magnetic nanoparticles, such as neodymium-iron-boron ($\text{Nd}_2\text{Fe}_{14}\text{B}$) magnetic nanoparticles, or encapsulated rare-earth magnetic nanoparticles, such as encapsulated $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles. Nano-sized magnetic particles result in a distinct advantage over micron-sized particles because the smaller nanoparticles have greater potential to form a single magnetic domain. Further, nano-sized magnetic particles are easier to align compared to micron-size particles. Additionally, in some embodiments, nano-sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic particles are used in an exchange spring magnet, for example as a hard magnet component.

[0044] Prior $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets were highly susceptible to oxidation of the neodymium, iron, and boron elements, limiting the durability and utility of the magnets. To withstand the corrosive effect of oxidation, the formed $\text{Nd}_2\text{Fe}_{14}\text{B}$ composites required a coating (such as nickel plating or rubber coating); however, the coating limits the utility of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets as the external coating prevents direct or near direct contact with other materials as required for some applications. Additionally, smaller $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles are particularly reactive, increasing the difficulty of forming magnetic composites with enhanced magnetic properties, such as exchange spring magnets.

[0045] Although nano-sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic particles are useful for enhancing the magnetic properties of composite permanent magnets, the nano-sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic

30

particles are more susceptible to oxidation and corrosion relative to micron-sized particles due to the increased surface to volume ratio of the smaller particles. The oxidation of the crystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ material results in decreased magnetization. The oxidation of magnetic particles is particularly problematic when forming composite permanent magnets, as oxidized nanoparticles
5 within the composite material results in a weakened permanent magnet. Additionally, oxidation can result in the corrosion of a composite magnet, causing cracking or crumbling of the magnet and a loss of magnetic strength.

[0046] What is needed in the field is a corrosion-resistant, high-strength $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet. However, to produce such a permanent magnet, corrosion of the individual particles, as
10 well as particle size, should be limited.

[0047] As described herein, encapsulating the magnetic particles with a protective layer can decrease the susceptibility of the particles to oxygenation, allowing the particles and composite magnets to retain their desired properties. Prior $\text{Nd}_2\text{Fe}_{14}\text{B}$ composite magnets could be coated with an outer protective layer, such as a metal plating, an epoxide layer, or a rubber layer.

15 However, such an outer coating fails to protect the individual particles, for example during the production of the composite magnet. During the formation of prior composite permanent magnets, individual particles would oxidize, thereby reducing the magnetic strength of the composite. Furthermore, any puncture or tear of the outer coating of the composite would result in the entire composite being compromised by oxidation. By coating individual $\text{Nd}_2\text{Fe}_{14}\text{B}$
20 nanoparticles, however, a chip or crack at the surface or other portion of the composite would not result in the entire composite being compromised. Additionally, the individually encapsulated particles are more resistant to oxidation during the formation of the magnet.

[0048] Encapsulated magnetic nanoparticles show an increased resistance to oxidation or corrosion compared to unencapsulated magnetic nanoparticles while minimizing magnetic
25 particle size. By being more resistant to oxidation or corrosion, encapsulated magnetic nanoparticles have increased lifespan and versatility for use as a permanent magnet.

[0049] In some embodiments, encapsulated magnetic nanoparticles are bonded together (such as by casting, cold pressing, or sintering (for example, spark plasma sintering)) to form a composite that can be used for any number of purposes that require permanent magnets, such as
30 motors, generators, computer hard disks (for example, head actuators), medical care (for example, magnetic resonance imaging or other diagnostic imaging techniques), or audio

equipment. In some embodiments, encapsulated metallic nanoparticle composites or rare earth nanoparticle composites are formed by pouring the nanoparticles into a mold and sintering or cold pressing the particles together. In some embodiments, nanoparticles are cold pressed or sintered to form a nanocomposite. In some embodiments, a magnetic field is applied to the nanoparticles during the cold pressing process to align the nanoparticles. In some embodiments, rare earth magnetic nanoparticle composites are molded or machined into a desired shape.

5 [0050] As used herein, the term "inert solvent" refers to any solvent that will not react with the magnetic nanoparticles described herein.

[0051] As used herein, a "rare earth magnetic nanoparticle" is any nanoparticle exhibiting magnetic property that includes one or more rare earth elements, including scandium, yttrium, 10 lanthanum, cerium, neodymium, samarium, praseodymium, dysprosium, terbium, promethium, europium, gadolinium, holmium, erbium, thulium, ytterbium, or lutetium.

[0052] The term "composite magnetic material" or "composite magnet" refers to any material comprising a plurality of magnetic particles. The term "nanocomposite magnetic material" or "nanocomposite magnet" refers to any material comprising a plurality of magnetic nanoparticles. 15

[0053] As used herein, the term "reduced" or "reduced state" of a material refers to all or substantially all of that material being in a metallic state. For example, in some embodiments, "reduced $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles" refers to $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles wherein all or substantially all of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticle material is in a metallic state.

20 [0054] The term "residue thereof" as used herein, refers to any material resulting from a precursor material as a result of any processing step, such as bonding particles together (which can occur, for example by pressing or sintering the particle). For example, when used to refer to a "nanoparticle core encapsulated by a protective layer or residue thereof," it is intended to refer to any nanoparticle that has a core encapsulated by a protective layer or the resulting nanoparticle, including the core and the residue of the encapsulating protective layer or 25 encapsulating protective reagent that results from any processing step.

[0055] When numerical values are expressed herein using the term "about" or the term "approximately," it is understood that both the value specified, as well as values reasonably close to the value specified, are included. For example, the description "about 50°C " or 30 "approximately 50°C " includes both the disclosure of 50°C itself, as well as values close to 50°C . Thus, the phrases "about X" or "approximately X" include a description of the value X itself. If

a range is indicated, such as "approximately 50°C to 60°C," it is understood that both the values specified by the endpoints are included, and that values close to each endpoint or both endpoints are included for each endpoint or both endpoints; that is, "approximately 50°C to 60°C" is equivalent to reciting both "50°C to 60°C" and "approximately 50°C to approximately 60°C."

5 [0056] By "substantially free of a specific component, a specific composition, a specific compound, or a specific ingredient in various embodiments, is meant that less than about 5 wt%, less than about 2 wt%, less than about 1 wt%, less than about 0.5 wt%, less than about 0.1 wt%, less than about 0.05 wt%, less than about 0.025 wt%, or less than about 0.01 wt% of the specific component, the specific composition, the specific compound, or the specific ingredient is present. Preferably, "substantially free of a specific component, a specific composition, a specific compound, or a specific ingredient indicates that less than about 1 wt% of the specific component, the specific composition, the specific compound, or the specific ingredient is present.

15 [0057] It is understood that reference to relative weight percentages in a composition assumes that the combined total weight percentages of all components in the composition add up to 100. It is further understood that relative weight percentages of one or more components may be adjusted upwards or downwards such that the weight percent of the components in the composition combine to a total of 100, provided that the weight percent of any particular component does not fall outside the limits of the range specified for that component.

20 [0058] This disclosure refers to both particles and powders. These two terms are equivalent, except for the caveat that a singular "powder" refers to a collection of particles. The present invention can apply to a wide variety of powders and particles. The terms "nanoparticle," "nanoparticle" and "nano-sized particle" are generally understood by those of ordinary skill in the art to encompass a particle on the order of nanometers in diameter, typically between about 0.5 nm to 100 nm, about 1 nm to 100 nm, about 1 nm to 50 nm, about 1 nm to about 30 nm, about 2 nm to about 20 nm, about 2 nm to about 10 nm, about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, the nanoparticles have an average grain size of about 50 nm or less, about 30 nm or less, or about 20 nm or less, or about 10 nm or less, or about 5 nm or less, or about 1 nm or less, or about 0.5 nm or less, or about 0.3 nm or less. In some embodiments, the nanoparticles have an average diameter of about 50 nm or less, about 30 nm or less, or about 20 nm or less, or about 10 nm or less, or about 5 nm or less, or about 1 nm or less, or about 0.5 nm

or less, or about 0.3 nm or less. In some embodiments, the aspect ratio of the particles, defined as the longest dimension of the particle divided by the shortest dimension of the particle, is between one and one hundred, or between one and ten, or between one and five, or between one and two. "Grain size" is measured using the ASTM (American Society for Testing and
5 Materials) standard (see ASTM E1 12 - 10). When calculating a diameter of a particle, the average of its longest and shortest dimension is taken; thus, the diameter of an ovoid particle with long axis 20 nm and short axis 10 nm would be 15 nm. The average diameter of a population of particles is the average of diameters of the individual particles, and can be measured by various techniques known to those of skill in the art.

10 [0059] This disclosure provides several embodiments. It is contemplated that any features from any embodiment can be combined with any features from any other embodiment. In this fashion, hybrid configurations of the disclosed features are within the scope of the present invention. As is appreciated by those of ordinary skill in the art, the protocols, processes, and procedures described herein can be repeated continuously or as often as necessary to satisfy the
15 needs described herein. Additionally, it is contemplated that certain method steps can be performed in alternative sequences to those disclosed.

[0060] In one embodiment, an encapsulated magnetic nanoparticle comprises a magnetic nanoparticle core encapsulated by a protective layer. In some embodiments, the magnetic nanoparticle is a metallic magnetic nanoparticle. In some embodiments, the magnetic
20 nanoparticle is a rare-earth magnetic nanoparticle. In some embodiments, the rare-earth magnetic nanoparticle comprises neodymium, iron, and boron. In some embodiments, the protective layer comprises a silane derivative. In some embodiments, the protective layer comprises phosphate. In some embodiments, the magnetic nanoparticle core is plasma generated. In some embodiments, the magnetic nanoparticle core is not produced by ball
25 milling.

[0061] Further described herein are permanent magnets. In one embodiment of a permanent magnet described herein, the permanent magnet comprises a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer or a residue thereof. In some embodiments, the magnetic
30 nanoparticle is a metallic magnetic nanoparticle. In some embodiments, the magnetic nanoparticle is a rare-earth magnetic nanoparticle. In some embodiments, the rare-earth

magnetic nanoparticle comprises neodymium, iron, and boron. In some embodiments, the protective layer comprises a silane derivative. In some embodiments, the protective layer comprises phosphate. In some embodiments, the magnetic nanoparticle core is plasma generated. In some embodiments, the magnetic nanoparticle core is not produced by ball
5 milling.

[0062] In one embodiment of a permanent magnet described herein, the permanent magnet is formed by bonding together a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer. In some embodiments, the magnetic nanoparticle is a metallic magnetic nanoparticle. In
10 some embodiments, the magnetic nanoparticle is a rare-earth magnetic nanoparticle. In some embodiments, the rare-earth magnetic nanoparticle comprises neodymium, iron, and boron. In some embodiments, the protective layer comprises a silane derivative. In some embodiments, the protective layer comprises phosphate. In some embodiments, the magnetic nanoparticle core is plasma generated. In some embodiments, the magnetic nanoparticle core is not produced by
15 ball milling.

[0063] Further describe herein are methods of making encapsulated magnetic nanoparticles, the method comprising suspending a plurality of magnetic nanoparticles in an inert solvent to form a dispersion, combining the dispersion with sodium borohydride, and combining the dispersion with a protective-layer reagent. In some embodiments, the magnetic nanoparticle is a
20 metallic magnetic nanoparticle. In some embodiments, the magnetic nanoparticle is a rare-earth magnetic nanoparticle. In some embodiments, the rare-earth magnetic nanoparticle comprises neodymium, iron, and boron. In some embodiments, the protective-layer reagent is a salinization reagent. In some embodiments, the protective-layer reagent is a phosphorylation reagent. In some embodiments, the method further comprises nano-sizing a plurality of micron-sized
25 magnetic particles to form the plurality of magnetic nanoparticles. In some embodiments, the nano-sizing step is performed using plasma. In some embodiments, the nano-sizing step is not performed by ball milling. In some embodiments, the method further comprises centrifuging the dispersion. In some embodiments, the method further comprises sonicating the dispersion. In some embodiments the method further comprises combining sodium hydroxide with the
30 dispersion. In some embodiments, the method further comprises washing the encapsulated

magnetic nanoparticles. In some embodiments, the method further comprises drying the encapsulated magnetic nanoparticles.

5 [0064] Further described herein is a method of making a permanent magnet comprising bonding together a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer. In some embodiments, the method further comprises combining a plurality of micron-sized magnetic particles with the plurality of encapsulated magnetic nanoparticles prior to the bonding step. In some embodiments, the magnetic nanoparticle is a metallic magnetic nanoparticle. In some embodiments, the magnetic nanoparticle is a rare-earth magnetic nanoparticle. In some 10 embodiments, the rare-earth magnetic nanoparticle comprises neodymium, iron, and boron. In some embodiments, the protective layer comprises a silane derivative. In some embodiments, the protective layer comprises phosphate. In some embodiments, the magnetic nanoparticle core is plasma generated. In some embodiments, the magnetic nanoparticle core is not produced by ball milling.

15 [0065] Also described herein is a method of making a permanent magnet comprising suspending a plurality of magnetic nanoparticles in an inert solvent to form a dispersion, combining the dispersion with sodium borohydride, combining the dispersion with a protective-layer reagent, thereby forming a plurality of encapsulated magnetic nanoparticles, and bonding together the plurality of encapsulated magnetic nanoparticles. In some embodiments, the method 20 further comprises combining a plurality of micron-sized magnetic particles with the plurality of encapsulated magnetic nanoparticles prior to the bonding step. In some embodiments, the magnetic nanoparticle is a metallic magnetic nanoparticle. In some embodiments, the magnetic nanoparticle is a rare-earth magnetic nanoparticle. In some embodiments, the rare-earth magnetic nanoparticle comprises neodymium, iron, and boron. In some embodiments, the method further comprises nano-sizing a plurality micron-sized magnetic particles to form the plurality of magnetic nanoparticles. In some embodiments, the nano-sizing step is performed using plasma. In some embodiments, the nano-sizing step is not performed by ball milling. In some embodiments, the method further comprises centrifuging the dispersion. In some 25 embodiments, the method further comprises sonicating the dispersion. In some embodiments the method further comprises combining sodium hydroxide with the dispersion. In some 30 embodiments, the method further comprises washing the encapsulated magnetic nanoparticles.

In some embodiments, the method further comprises drying the encapsulated magnetic nanoparticles. In some embodiments, the method comprises cold pressing the encapsulated magnetic nanoparticles. In some embodiments, the method comprises sintering the encapsulated magnetic nanoparticles.

5

Magnetic Nanoparticles

[0066] Magnetic nanoparticles are encapsulated to produce encapsulated magnetic nanoparticles as described herein. In some embodiments, metallic magnetic nanoparticles are encapsulated to produce encapsulated metallic magnetic nanoparticles. In some embodiments, 10 rare-earth magnetic nanoparticles are encapsulated to produce encapsulated rare-earth magnetic nanoparticles. Generally, the magnetic nanoparticles are initially formed under reducing conditions. In some embodiments, magnetic nanoparticles are plasma generated. In some embodiments, the magnetic nanoparticles are not produced by ball milling.

[0067] The magnetic nanoparticles described herein are generally directed to rare-earth 15 magnetic nanoparticles, particularly $\text{Nd}_2\text{Fe}_{10}\text{B}$ nanoparticles, but it is understood that other magnetic nanoparticles, including any metallic magnetic nanoparticle or other rare-earth magnetic nanoparticles, can be similarly made or used. A "rare earth magnetic nanoparticle" is any nanoparticle exhibiting magnetic property that includes one or more rare earth elements, including scandium, yttrium, lanthanum, cerium, neodymium, samarium, praseodymium, 20 dysprosium, terbium, promethium, europium, gadolinium, holmium, erbium, thulium, ytterbium, or lutetium. For example, in some embodiments, the rare earth magnetic nanoparticle comprises any neodymium alloy (such as $\text{Nd}_2\text{Fe}_{10}\text{B}$) or samarium alloy (such as samarium-cobalt alloy). In some embodiments, rare earth magnetic nanoparticles further comprises other elements, including, but not limited to, carbon, cobalt, copper, dysprosium, gallium, iron, niobium, zinc, or 25 zirconium. In some embodiments, a rare earth element comprises less than 5% of the atoms in a rare earth magnetic nanoparticle, less than 10% of the atoms in a rare earth magnetic nanoparticle, or less than 15% of the atoms in a rare earth magnetic nanoparticle, less than 20% of the atoms in a rare earth magnetic nanoparticle, less than 25% of the atoms in a rare earth magnetic nanoparticle, or less than 30% of the atoms in a rare earth magnetic particles. In some 30 embodiments, a rare earth element comprises more than 1% of the atoms in a rare earth magnetic nanoparticle, more than 5% of the atoms in a rare earth magnetic nanoparticle, or more than 10%

of the atoms in a rare earth magnetic nanoparticle, or more than 15% of the atoms in a rare earth magnetic nanoparticle, more than 20% of the atoms in a rare earth magnetic nanoparticle, or more than 25% of the atoms in a rare earth magnetic nanoparticle.

[0068] In some embodiments rare-earth magnetic nanoparticles comprise neodymium, iron, and boron, preferably at a molar ratio of 2:14:1 Nd:Fe:B (that is, Nd₂Fe₁₄B). Preferably, the Nd₂Fe₁₄B nanoparticles are about 26.7 % neodymium by weight, about 72.3% iron by weight, and about 1% boron by weight. In some embodiments, the rare-earth magnetic nanoparticles comprise about 24% to about 28% neodymium by weight excluding any oxygen, or about 25% to about 27% neodymium by weight excluding any oxygen. In some embodiments, the rare-earth magnetic nanoparticles comprise about 70% to about 74% iron by weight excluding any oxygen, or about 72% to about 73% iron by weight excluding any oxygen. In some embodiments, the rare-earth magnetic nanoparticles comprise 0.5% to about 1.5% boron by weight excluding any oxygen. In some embodiments, the rare-earth magnetic nanoparticles comprise an additional element, such as, but not limited to, carbon, cobalt, copper, dysprosium, gallium, iron, niobium, zinc, or zirconium. For example, in some embodiments, the rare-earth magnetic nanoparticles comprise about 0% to about 2% niobium by weight excluding any oxygen, or about 0.8% to about 1.8% niobium by weight excluding any oxygen, or about 0.8% to about 1.2% niobium by weight excluding any oxygen, or about 1% niobium by weight excluding any oxygen.

[0069] In some embodiments, all or substantially all of the atoms of the magnetic nanoparticles are in a metallic state. In some embodiments, the magnetic nanoparticles are essentially free of oxidized species. In some embodiments, all or substantially all of the atoms of the rare-earth magnetic nanoparticles are in a metallic state. In some embodiments, the rare-earth magnetic nanoparticles are essentially free of oxidized species. In some embodiments, all or substantially all of the atoms of the Nd₂Fe₁₄B magnetic nanoparticles are in a metallic state. In some embodiments, the Nd₂Fe₁₄B magnetic nanoparticles are essentially free or substantially free of oxidized species. In some embodiments, less than about 5% of surface atoms are oxidized, less than about 10% of surface atoms are oxidized, less than about 15% of surface atoms are oxidized, less than about 25% of surface atoms are oxidized, less than about 35% of surface atoms are oxidized, or less than about 50% of surface atoms are oxidized. In some

embodiments, X-ray photoelectron spectroscopy (XPS) is used to determine the presence of oxidized material.

[0070] In some embodiments, the magnetic nanoparticles are between about 2 nm and about 20 nm, or between about 2 nm and about 15 nm, or between about 1 nm and about 10 nm, or
5 between about 3 nm and about 5 nm. In some embodiments, about 80% or more of the magnetic nanoparticles are between about 2 nm and about 20 nm, or between about 2 nm and about 15 nm, or between about 1 nm and about 10 nm, or between about 3 nm and about 5 nm. In some
10 embodiments, about 90% or more of the magnetic nanoparticles are between about 2 nm and about 20 nm, or between about 2 nm and about 15 nm, or between about 1 nm and about 10 nm, or between about 3 nm and about 5 nm. In some embodiments, about 95% or more of the magnetic nanoparticles are between about 2 nm and about 20 nm, or between about 2 nm and
15 about 15 nm, or between about 1 nm and about 10 nm, or between about 3 nm and about 5 nm. In some embodiments, the magnetic nanoparticles have an aspect ratio between one and one hundred, or between one and ten, or between one and five, or between one and two, or between one and 1.5, or about one. In some embodiments, about 80% or more of the magnetic nanoparticles have an aspect ratio between one and one
20 hundred, or between one and ten, or between one and five, or between one and two, or between one and 1.5, or about one. In some embodiments, about 90% or more of the magnetic nanoparticles have an aspect ratio between one and ten, or between one and five, or between one and two, or between one and 1.5, or about one. In some embodiments, about 95% or more of the magnetic nanoparticles have an aspect ratio between one and ten, or between one and five, or
25 between one and two, or between one and 1.5, or about one. In some embodiments, about 99% or more of the magnetic nanoparticles have an aspect ratio between one and ten, or between one and five, or between one and two, or between one and 1.5, or about one.

[0071] Prior attempts at obtaining $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles have been met with significant challenge, as the increased surface area of nanoparticles relative to micron-sized particles results in a substantial increase in the reactivity of the particles to oxygen. Oxidization of the particles
30 results a loss of magnetic properties and increased corrosion. Accordingly, in some prior

attempts at forming $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic particles, the particles were oxidized prior to successful processing into a composite magnet, thus resulting in a suboptimal composite magnet.

[0072] Additionally, some prior attempts at forming magnetic nanoparticles have resulted in non-preferred sizes or morphologies. For example, in some prior attempts at forming $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles by ball-milling larger micron-sized particles results in the formation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ plates rather than rounder particles. Preferably the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic particles are spheres, although other morphologies, including plates, squares, cubic, or tetragonal, are contemplated. Furthermore, the high energy input required to ball-mill micron-sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles to produce $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles is impractical to produce $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles, particularly in large scale. Accordingly, in some embodiments, the magnetic nanoparticles, rare-earth magnetic nanoparticles, or $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles are not produced by ball milling.

[0073] In some embodiments, magnetic nanoparticles, such as metallic magnetic nanoparticles or rare-earth magnetic nanoparticles (such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles), are plasma generated, for example by feeding a mixture of neodymium, iron, and boron materials into a plasma system, such those described in US 2014/0263 190, or by similar techniques to those described in US 5,989,648, US 6,689,192, US 6,755,886, and US 2005/0233380, the disclosures of which are herein incorporated by reference. Plasma-generated particles provide a distinct advantage over other particle production methods because the plasma-generated particles are more consistently sized, more consistently shaped, and surface oxidation of the particles can be more easily controlled by controlling the plasma generated environment. Nevertheless, other methods of magnetic nanoparticle production are contemplated.

[0074] In some embodiments, magnetic materials (for example, magnetic materials comprising neodymium, iron, or boron, or magnetic metals, magnetic alloys, or magnetic metal alloys) are fed into the plasma reactor to produce the magnetic nanoparticles (such as metallic magnetic nanoparticles or rare-earth magnetic nanoparticles, for example $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles). In some embodiments, the neodymium, iron, and boron are separate feed materials, while in some embodiments a single feed material (for example a single feed material comprising neodymium, iron, boron, or combinations thereof) is used. For example, in some embodiments, micron-sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles are used as feed material. In some embodiments, the neodymium, iron, or boron materials are micron-sized powders, for example particles that are about 0.2 microns to about 10 microns in diameter, about 0.3 microns to about 6 microns, or about 0.5 microns to

about 4 microns. In some embodiments, the neodymium, iron, or boron materials are provided to the plasma reactor as a liquid or slurry.

[0075] In some embodiments, the feed material comprises magnetic material, for example neodymium, iron, and boron, or magnetic metals, magnetic alloys, or magnetic metal alloys. In some embodiments, the feed material comprises one or more additional elements, for example, but not limited to, carbon, cobalt, copper, dysprosium, gallium, iron, niobium, zinc, or zirconium. For example, in some embodiments, micron-sized particles comprising neodymium, iron, boron, and niobium are used as feed material. In some embodiments, the feed material comprises about 24% to about 28% neodymium by weight excluding any oxygen, or about 25% to about 27% neodymium by weight excluding any oxygen. In some embodiments, the feed material comprises about 70% to about 74% iron by weight excluding any oxygen, or about 72% to about 73% iron by weight excluding any oxygen. In some embodiments, the feed material comprises 0.5% to about 1.5% boron by weight excluding any oxygen. In some embodiments, the feed material comprises about 0% to about 2% niobium by weight excluding any oxygen, or about 0.8% to about 1.8% niobium by weight excluding any oxygen, or about 0.8% to about 1.2% niobium by weight excluding any oxygen, or about 1% niobium by weight excluding any oxygen. In some embodiments, the approximate weight proportions of each element can be determined by using atomic emission spectroscopy, for example inductively coupled plasma atomic emission spectroscopy.

[0076] Plasma generation and particle production generally occurs in a non-oxidative environment. A working gas, such as argon, is supplied to the plasma gun for the generation of plasma. Preferably, the working gas further comprises a reducing gas, such as H₂. In one embodiment, an argon/hydrogen mixture (in the ratio of 10:1 Ar/H₂) is used as the working gas. In some embodiments, the presence of H₂ gas provides reducing conditions for the production of the magnetic nanoparticles. For example, the H₂ gas can react with a portion of the residual oxygen in the system, thereby limiting the amount of oxidized material present in the produced magnetic nanoparticles. In some embodiments, the amount of oxygenated species in the resulting magnetic nanoparticles can be tuned by adjusting the amount of H₂ gas in the system. Magnetic materials, such as neodymium, iron, or boron materials, or magnetic metals, magnetic alloys, or magnetic metal alloys, are rapidly vaporized or turned into plasma after being introduced into the plasma reactor. The kinetic energy of the superheated material, which can

reach temperatures of 20,000 to 30,000 Kelvin, ensures thorough mixing of all components. The superheated material of the plasma stream is then rapidly quenched using such methods as the turbulent quench chamber disclosed in US 2008/0277267, the disclosure of which is hereby incorporated by reference. Argon quench gas at high flow rates, such as 2400 to 2600 liters per minute, is injected into the superheated material to aid the quenching processes. The material is then further cooled in a cool-down tube, and collected and analyzed to ensure proper size ranges of material.

[0077] Preferably, the rare-earth magnetic nanoparticles are retained under inert conditions (for example, under argon) or reducing conditions (for example under hydrogen or under a mixture of argon and hydrogen). In some embodiments, the rare-earth magnet nanoparticles are suspended and retained in an inert solvent, for example methanol, ethanol, or isopropanol. The resulting particles can be used for any purpose, or can be further processed by encapsulating the rare-earth magnetic nanoparticles, as described below.

15 *Encapsulated Magnetic Nanoparticles*

[0078] Magnetic nanoparticles, for example, metallic magnetic nanoparticles or rare-earth magnetic nanoparticles (such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles), can be used to produce magnetic composites, which can be used for a variety of industrial purposes. However, due to the high surface area of certain magnetic nanoparticles, such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles, the particles are particularly pyrophoric and subject to oxidation when exposed to air. As described herein, to limit exposure of the particles to oxidizing compounds the rare earth magnetic nanoparticles are encapsulated by various materials. Encapsulated magnetic nanoparticles described herein are generally directed to encapsulated rare-earth magnetic nanoparticles (particularly $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles), but it is understood that other encapsulated magnetic nanoparticles can be similarly made or used.

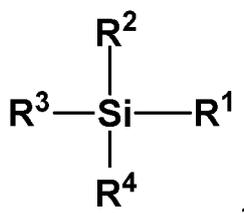
[0079] For encapsulated magnetic nanoparticles as described herein, protective layer reagents covalently bind the surface of magnetic nanoparticles cores, forming a protective layer and shielding the nanoparticle core from some or all ambient oxidizing compounds. In some embodiments, the encapsulated magnetic nanoparticles are less reactive or susceptible to corrosion compared to unencapsulated magnetic nanoparticles, and can be used to form composite magnets. The composite magnets described herein can be shaped or molded for

various purposes. In some embodiments, the magnetic nanoparticle cores described herein are rare-earth magnetic nanoparticles, such as Nd₂Fe₄B nanoparticles. In some embodiments, the protective layer comprises a silane derivative. In some embodiments, the protective layer comprises a phosphate group.

5 [0080] Encapsulated magnetic nanoparticles comprise a magnetic nanoparticle core (such as a rare-earth magnetic nanoparticle core or metallic magnetic nanoparticle core) encapsulated by a protective layer. A protective-layer reagent is used to form the protective layer. In some
 10 embodiments, the protective-layer reagent is a silanization reagent, which is used to form a protective layer comprising a silane-derivative. In some embodiments, the protective-layer reagent is a phosphorylation reagent, which is used to form a protective layer comprising
 phosphate.

[0081] In one preferred embodiment, encapsulation of the magnetic nanoparticles, such as the rare-earth magnetic nanoparticles (for example, Nd₂Fe₄B nanoparticles) or metallic magnetic nanoparticles, is accomplished by silanization of the surface of the nanoparticles. Typically, the
 15 nanoparticle surface is treated with strong base, for example, a hydride base such as sodium borohydride, followed by reaction with one or more silanization reagents. While not wishing to be bound by theory, it is currently hypothesized that the silanization reagents react with trace oxidized species on the surface of the Nd₂Fe₄B nanoparticles (that is, while the Nd₂Fe₄B nanoparticles are substantially free of oxidized species, sufficient traces of oxidized species
 20 remain on the surface of the nanoparticles to enable bonding of the silanization reagent).

[0082] In one embodiment, the nanoparticles, such as Nd₂Fe₄B nanoparticles, are silanized using a reagent of Formula I:



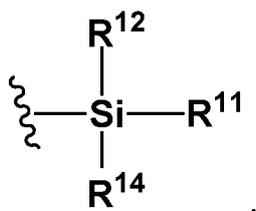
25

Formula I

wherein R¹ is a hydrophobic group; for example, R¹ can be selected from the group consisting of C₂-C₁₈ alkyl; R² and R⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo; and R³ is a leaving group. In one embodiment, R¹

is selected from the group consisting of C₆-C₈ alkyl; in another embodiment, R¹ is C₈ alkyl, such as n-octyl. R³ can be selected from the group consisting of halogens, iodo, bromo, chloro, or sulfonate. In another embodiment, R² and R⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro, and R³ is a leaving group, such as chloro. In another embodiment, R² and R⁴ are both -CH₃ and R³ is chloro. In another embodiment, R² is -CH₃, R⁴ is chloro, and R³ is chloro. In another embodiment, R² and R⁴ are both -OCH₃ and R³ is chloro. In another embodiment, R² is -OCH₃, R⁴ is chloro, and R³ is chloro. In another embodiment, R² and R⁴ are both -CH₂CH₃ and R³ is chloro. In another embodiment, R² is -CH₂CH₃, R⁴ is chloro, and R³ is chloro. In another embodiment, R² and R⁴ are both -OCH₂CH₃ and R³ is chloro. In another embodiment, R² is -OCH₂CH₃, R⁴ is chloro, and R³ is chloro. In another embodiment, R², R³, and R⁴ are all chloro. In any of the foregoing embodiments, R¹ can be C₈ alkyl, such as n-octyl. In some embodiments, the silane reagent is an organosilane, an organochlorosilane, or an organodichlorosilane. In some embodiments, the silanization reagent is dichloromethyl octylsilane.

15 [0083] In some embodiments, the encapsulated metallic magnetic particles or encapsulated rare-earth magnetic nanoparticles are bonded to any number of silane derivatives, thereby producing a rare earth magnetic nanoparticle core encapsulated by a silane derivative protective layer. In some embodiments, Nd₂Fe₁₄B nanoparticles are bonded to a silane derivative. In some embodiments, the silane derivative is of the formula:



20 Formula II

wherein R¹¹ is a hydrophobic group; for example, R¹¹ can be selected from the group consisting of C₂-C₈ alkyl or C₃-C₈ n-alkyl; and R¹² and R¹⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo. In one embodiment, R¹¹ is selected from the group consisting of C₆-C₈ alkyl; in another embodiment, R¹¹ is C₈ alkyl, such as n-octyl. In another embodiment, R¹² and R¹⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro. In another embodiment, R¹² and R¹⁴ are both -CH₃. In another embodiment, R¹² is -CH₃ and R¹⁴ is chloro. In another

embodiment, R¹² and R¹⁴ are both -OCH₃. In another embodiment, R¹² is -OCH₃, and R¹⁴ is chloro. In another embodiment, R¹² and R¹⁴ are both -CH₂CH₃. In another embodiment, R¹² is -CH₂CH₃ and R¹⁴ is chloro. In another embodiment, R¹² and R¹⁴ are both -OCH₂CH₃. In another embodiment, R¹² is -OCH₂CH₃ and R¹⁴ is chloro. In another embodiment, R¹² and R¹⁴ are both chloro. In any of the foregoing embodiments, R¹¹ can be C₈ alkyl, such as n-octyl.

[0084] In some embodiments, the silane derivatives encapsulate the magnetic nanoparticle. In some embodiments, the silane derivatives form a protective layer configured to protect the magnetic nanoparticle from oxygenating compounds. In some embodiments, the protective layer of the magnetic nanoparticle is about 0.5 nm thick or less, about 1 nm thick or less, about 2 nm thick or less, or about 5 nm thick or less.

[0085] In some embodiments, an encapsulated rare-earth magnetic nanoparticle is encapsulated by a phosphate-containing protective layer. In some embodiments, the surface of the rare-earth magnetic nanoparticle is phosphorylated by reacting the rare-earth magnetic nanoparticles (such as Nd₂Fe₁₄B nanoparticles) with a phosphorylation reagent, for example phosphoric acid. Typically, the nanoparticle surface is treated with strong base, for example, a hydride base such as sodium borohydride, followed by reaction with phosphoric acid.

[0086] In some embodiments, the encapsulated magnetic nanoparticles have an average diameter or average grain size of about 100 nm or less, about 50 nm or less, about 30 nm or less, about 20 nm or less, about 10 nm or less, about 5 nm or less, about 3 nm or less, or about 2 nm or less. In some embodiments, the encapsulated magnetic nanoparticles have an average diameter or average grain size of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, the encapsulated magnetic nanoparticles are approximately spherical. In some embodiments, the encapsulated magnetic nanoparticles are rod-shaped. In some embodiments, the encapsulated magnetic nanoparticles have an aspect ratio is between one and one hundred, or between one and ten, or between one and two.

[0087] One embodiment of an encapsulated magnetic nanoparticle is illustrated in FIG. 1, a magnetic nanoparticle core 110 is bonded to a plurality of organosilane derivatives 120, such as octylsilane. The organosilane encapsulation prevents oxidizing compounds from reaching the surface of the magnetic nanoparticle core 110, decreasing reactivity of the nanoparticle core.

Without being bound by theory, it is currently hypothesized that one or more oxidized atoms on the surface of the magnetic nanoparticle core 110, for example, oxidized iron on the surface of a $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticle core, binds to the silane derivative 120 via a X—O—Si bond (where X is an oxidizable surface atom). That is, while the magnetic nanoparticles are substantially free of oxidized species, sufficient traces of oxidized species can remain on the surface of the nanoparticles to enable bonding of the silanization reagent. In some embodiments, an $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticle core binds to a silane derivative via a Fe—O—Si bond. In some embodiments, a single silane derivative 120 is bound to the magnetic nanoparticle core 110 by one X—O—Si bond. In some embodiments, a single silane 120 derivative is bound to the magnetic nanoparticle core 110 by two X—O—Si bonds. In some embodiments, a silane derivative 120 is bound to both the magnetic nanoparticle core 110 via a X—O—Si bond and to another silane derivative 120 via a Si—O—Si bond. In some embodiments, a silane derivative 120 is bound to two different silane derivatives 120 via Si—O—Si bonds. In some embodiments, the oxide bond to the silicon atom is formed by replacing one or more functional groups, for example a chloro group.

[0088] Preferably, the encapsulated magnetic nanoparticles are essentially free of non-protective-layer-conjugated oxidative species. Nevertheless, in some embodiments, a portion of surface atoms of the magnetic nanoparticle core are oxidized, even after encapsulation. For example, in some embodiments, about 10% or less of the non-protective-layer-conjugated core surface atoms are oxidized, about 5% or less of the non-protective-layer-conjugated core surface atoms are oxidized, about 3% or less of the non-protective-layer-conjugated core surface atoms are oxidized, about 1% or less of the non-protective-layer-conjugated core surface atoms are oxidized, about 0.5% or less of the non-protective-layer-conjugated core surface atoms are oxidized, about 0.25% or less of the non-protective-layer-conjugated core surface atoms are oxidized, about 0.1% or less of the non-protective-layer-conjugated core surface atoms are oxidized, or about 0.05% or less of the non-protective-layer-conjugated core surface atoms are oxidized. In some embodiments, X-ray photoelectron spectroscopy (XPS) is used to determine the presence of oxidized material. Nevertheless, the encapsulating protective layer serves to reduce the amount of magnetic nanoparticle core surface oxidized atoms relative to unencapsulated magnetic nanoparticles.

[0089] In some embodiments, the encapsulated magnetic nanoparticles are stored under inert conditions, such as in an inert solvent (for example, an alcohol, such as methanol, ethanol, or isopropanol) or under an inert gas, such as argon. In some embodiments, the encapsulated magnetic nanoparticles are used to form a composite, for example by sintering or cold pressing
5 the particles to form a larger magnetic composite. In some embodiments, the encapsulated magnetic nanoparticles are placed into a mold prior to cold pressing or sintering, forming a desired shape. In some embodiments, the encapsulated magnetic nanoparticle composite is machined into a desired shape after cold pressing or sintering.

[0090] In some embodiments, magnets formed using encapsulated magnetic nanoparticles
10 have increased resistance to oxygenation, increasing their lifespan and utility. In some embodiments oxidation of encapsulated magnetic nanoparticles can be monitored by any method, for example by X-ray photoelectron spectroscopy.

[0091] Permanent magnets comprising encapsulated nanoparticles can be used for any variety of purposes for which a permanent magnet would be desirable. In some embodiments,
15 encapsulated magnetic nanoparticles can be used in motors, such as permanent magnet synchronous motors or asynchronous motors, or motor components, such as in stators or rotors. For example, some prior motors require a small air gap between a stator and a rotor, which might result in oxidation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet. In some embodiments, the motors using encapsulated magnetic nanoparticles are deployed in, for example, vehicles, medical devices,
20 power tools, servomotors, or actuators. By employing encapsulated magnetic nanoparticles, however, the permanent magnet in the motor is more resistant to corrosion.

[0092] In some embodiments, encapsulated magnetic nanoparticles are employed in motors, generators, such as a permanent magnet synchronous generator, steam turbines, gas turbines, wind turbines, hydro turbines, or reciprocating engines. In some embodiments, encapsulated
25 magnetic nanoparticles are employed in magnetic resonance imaging systems or other spectroscopy techniques including, but not limited to, nuclear magnetic resonance (NMR) spectroscopy, magnetic probes (for example in bioimaging or therapeutic applications including, but not limited to contrast agents or localized drug delivery systems).

[0093] In some embodiments, encapsulated magnetic nanoparticles are used in computer
30 hardware, for example in computer hard disks (such as a head actuator). In some embodiments,

encapsulated magnetic magnets are used in audio equipment, for example in speakers, headphones, or microphones.

Production of Encapsulated Magnetic Nanoparticles

5 [0094] Magnetic nanoparticles encapsulated using the methods described herein are generally directed to encapsulated rare-earth magnetic nanoparticles, particularly encapsulated $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles, but it is understood that other encapsulated magnetic nanoparticles can be similarly made or used, such as encapsulated metallic magnetic nanoparticles.

[0095] Encapsulated magnetic nanoparticles are produced by suspending magnetic
10 nanoparticles, such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles as described above, in an inert solvent, producing a suspension. The inert solvent should not react with either the magnetic nanoparticles used to encapsulate the nanoparticles. In some embodiments, the inert solvent is an alcohol. Preferably, the inert solvent is isopropanol or methanol; however, any other inert solvent is contemplated, such as ethanol, butanol, other alcohols, acetone, chloroform, or ethyl acetate. In some
15 embodiments, the inert solvent is at least 95% pure, or at least 98% pure, or at least 99% pure. In some embodiments, the inert solvent is anhydrous or approximately anhydrous. In some embodiments, the rare-earth magnetic nanoparticles are under reducing or inert conditions prior to being suspended by the inert solvent, for example under nitrogen gas, argon gas, hydrogen gas, a mixture of hydrogen gas and argon gas, or a mixture of hydrogen gas and nitrogen gas. In
20 some embodiments, the inert solvent is purged of oxygenated gases by flowing nitrogen gas or argon gas through the solvent prior to use. Other inert gases may be used, for example argon.

[0096] In some embodiments, the magnetic nanoparticle suspension is sonicated to ensure an approximately uniform dispersion of particles. In some embodiments, the magnetic nanoparticle suspension is centrifuged to separate larger particles, for example micron-sized particles, from
25 the dispersion. In some embodiments, pelleted larger particles are disposed, for example particles about 5 nm or more, about 10 nm or more, about 20 nm or more, about 30 nm or more, about 50 nm or more, about 100 nm or more, about 200 nm or more, about 300 nm or more, about 500 nm or more, or about 1 micron or more. In some embodiments, about 99% or more of magnetic nanoparticles in the suspension have an average diameter or average grain size of about
30 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm

to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, about 98% or more of the magnetic nanoparticles in the suspension have an average diameter or average grain size of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, about 95% or more of the magnetic nanoparticles in the suspension have an average diameter or average grain size of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, about 90% or more of the magnetic nanoparticles in the suspension have an average diameter or average grain size of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm.

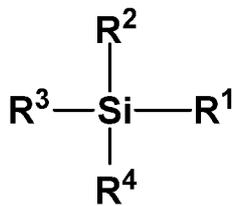
[0097] In some embodiments, sodium hydroxide is also added to the suspension, for example from about 0.01% to about 0.1% sodium hydroxide by weight, about 0.03% to about 0.08% sodium hydroxide by weight, or about 0.05% sodium hydroxide by weight. In some embodiments, about 0.08 grams to about 0.8 grams sodium hydroxide is added to about 800 grams of solvent, or about 0.24 grams to about 0.64 grams sodium hydroxide is added to about 800 grams of solvent, or about 0.4 grams of sodium hydroxide is added to about 800 grams of solvent.

[0098] In some embodiments, a strong base, preferably sodium borohydride (NaBH_4) is added to the suspension at a molar ratio of about 1:10 to about 5:1 $\text{NaBH}_4:\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 1:5 to about 5:1 $\text{NaBH}_4:\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 1:2 to about 2:1 $\text{NaBH}_4:\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 1:1 $\text{NaBH}_4:\text{Nd}_2\text{Fe}_{14}\text{B}$. In some embodiments, about 0.45 grams (0.012 moles) NaBH_4 to about 22.7 grams (0.6 moles) NaBH_4 is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 0.91 grams (0.024 moles) NaBH_4 to about 22.7 grams (0.6 moles) NaBH_4 is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 2.3 grams (0.06 moles) NaBH_4 to about 9.1 grams (0.24 moles) NaBH_4 is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 4.5 grams (0.12 moles) is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$.

[0099] A protective layer reagent is then added to the suspension to encapsulate the rare-earth magnetic nanoparticles. In some embodiments, the protective layer reagent is a silanization reagent. In some embodiments, the protective layer reagent is a phosphorylation reagent. In some embodiments, protective layer reagent is added to the suspension, for example at a molar ratio of about 10:1 to about 1:2 protective layer reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$, or 5:1 to about 1:1 protective layer reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 3:1 to about 1:1 protective layer reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 2:1 protective layer reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$. The protective layer reagent reacts with the sodium borohydride-treated magnetic nanoparticles to encapsulate the magnetic nanoparticles. Preferably, the reaction occurs while mixing the nanoparticle dispersion. In some embodiments, the reaction occurs at about 15 °C to about 30 °C, or about 20 °C to about 25 °C. In some embodiments, the reaction allowed to proceed for about 10 minutes to about 60 minutes, or about 15 minutes to about 45 minutes, or about 30 minutes.

[0100] In some embodiments, a silanization reagent, such as an organosilane or organochlorosilane derivative, preferably dichloromethyloctylsilane (DCMOS), is added to the nanoparticle suspension. Additional silanization reagents are discussed above. In some embodiments, for example, the silanization reagent is added to the magnetic nanoparticles at a molar ratio about 5:1 to about 1:2 silanization reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 3:1 to about 1:1 silanization reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 2:1 silanization reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$. In some embodiments, about 14 grams to about 138 grams of a silanization reagent is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 28 grams to about 83 grams of a silanization reagent is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 55 grams of a silanization reagent is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$.

[0101] In some embodiments, the silanization reagent has a formula according to Formula I:



Formula I

5 wherein R¹ is a hydrophobic group; for example, R¹ can be selected from the group consisting of C₂-C₁₈ alkyl; R² and R⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo; and R³ is a leaving group. In one embodiment, R¹ is selected from the group consisting of C₆-C₈ alkyl; in another embodiment, R¹ is C₈ alkyl, such as n-octyl. R³ can be selected from the group consisting of halogens, for example, chloro and
 10 bromo, more preferably chloro. In another embodiment, R² and R⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro, and R³ is a leaving group, such as chloro. In another embodiment, R² and R⁴ are both -CH₃ and R³ is chloro. In another embodiment, R² is -CH₃, R⁴ is chloro, and R³ is chloro. In another embodiment, R² and R⁴ are both -OCH₃ and R³ is chloro. In another embodiment, R² is -OCH₃, R⁴ is chloro, and
 15 R³ is chloro. In another embodiment, R² and R⁴ are both -CH₂CH₃ and R³ is chloro. In another embodiment, R² is -CH₂CH₃, R⁴ is chloro, and R³ is chloro. In another embodiment, R² and R⁴ are both -OCH₂CH₃ and R³ is chloro. In another embodiment, R² is -OCH₂CH₃, R⁴ is chloro, and R³ is chloro. In another embodiment, R², R³, and R⁴ are all chloro. In any of the foregoing embodiments, R¹ can be C₈ alkyl, such as n-octyl. In some embodiments, the silane reagent is an
 20 organosilane, an organochlorosilane, or an organodichlorosilane. In some embodiments, the silanization reagent is dichloromethyl octylsilane.

[0102] In some embodiments, the silanization reagent is added to the suspension after the sodium borohydride is dispersed throughout the dispersion. The silanization reagent reacts with the sodium borohydride-treated Nd₂Fe₄B nanoparticles to encapsulate the Nd₂Fe₄B
 25 nanoparticles. Preferably, the reaction occurs while mixing the nanoparticle suspension. In some embodiments, the reaction occurs at about 15 °C to about 30 °C, or about 20 °C to about 25 °C. In some embodiments, the reaction allowed to proceed for about 10 minutes to about 60 minutes, or about 15 minutes to about 45 minutes, or about 30 minutes. In some embodiments,

the $\text{Nd}_2\text{Fe}_{14}\text{B}$ core attaches to the silanization reagent via the silicon atom of the silane derivative by replacing a functional group of the unbound molecule, for example a chloro group.

[0103] In some embodiments, a phosphorylation reagent, such as phosphoric acid, is added to the nanoparticle suspension at a molar ratio of about 5:1 to about 1:2 phosphorylation reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 3:1 to about 1:1 phosphorylation reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 2:1 phosphorylation reagent: $\text{Nd}_2\text{Fe}_{14}\text{B}$. In some embodiments, about 5.9 grams to about 59 grams of a phosphorylation reagent is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 12 grams to about 35 grams phosphorylation reagent is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$, or about 24 grams of a phosphorylation reagent is added to a suspension comprising about 130 grams (0.12 moles) $\text{Nd}_2\text{Fe}_{14}\text{B}$. In some embodiments, the phosphorylation reagent is added to the suspension after the sodium borohydride is dispersed throughout the suspension. The phosphorylation reagent reacts with the sodium borohydride-treated $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles to encapsulate the $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles with a phosphate-containing protective layer. Preferably, the reaction occurs while mixing the nanoparticle suspension. In some embodiments, the reaction occurs at about 15 °C to about 30 °C, or about 20 °C to about 25 °C. In some embodiments, the reaction allowed to proceed for about 10 minutes to about 60 minutes, or about 15 minutes to about 45 minutes, or about 30 minutes.

[0104] In some embodiments, the encapsulated magnetic nanoparticles are separated from the solvent by ultracentrifugation. The supernatant is removed from the settled encapsulated magnetic nanoparticles by any method, for example decanting or siphoning. In some embodiments, the encapsulated magnetic nanoparticles are washed to reduce any remaining reaction impurities by suspending in an inert solvent to produce a colloid, mixing the colloid, centrifuging the colloid, and removing the supernatant solvent. In some embodiments, any inert solvent is used to wash the encapsulated nanoparticles, for example isopropanol, ethanol, or methanol. In some embodiments, the suspension is mixed for at least 3 minutes, or at least 5 minutes, or at least 10 minutes. This process of suspending, centrifuging, mixing and removing solvent can be repeated as many times as desired to obtain the intended purity of encapsulated magnetic nanoparticles. In some embodiments, the encapsulated nanoparticles are washed two or more times, three or more times, or four or more times.

[0105] In some embodiments, the encapsulated magnetic nanoparticles are dried, for example for example by warming the precipitate (for example, at about 30°C to about 70°C, about 30°C to about 60°C, at atmospheric pressure or at reduced pressure such as from about 1 pascal to about 90,000 pascal) for 12 hours or more, 24 hours or more, or 36 hours or more. Alternatively, in
5 some embodiments, the precipitate is freeze-dried. In some embodiments, the dried encapsulated magnetic nanoparticles are then be poured into a mold and cold pressed and/or sintered (for example, by spark-plasma sintering) together to form a larger magnet.

[0106] In some embodiments, the encapsulated magnetic nanoparticles are stored under an inert gas, for example argon or nitrogen. In some embodiments, encapsulated magnetic
10 nanoparticles are stored in an inert solvent, for example isopropanol, ethanol, or methanol. In some embodiments, for encapsulated magnetic nanoparticles stored in an inert solvent, the particles are later dried and used to form magnetic particles. In some embodiments, the nanoparticles are used as dispersion, suspended in the inert solvent.

15 *Nanocomposite Magnetic Materials*

[0107] The encapsulated magnetic nanoparticles described herein can be used to form permanent magnets. In some embodiments, the encapsulated magnetic nanoparticles are bonded or sintered together to form a permanent magnet. In some embodiments, a permanent magnet comprises additional particles, for example magnetic or non-magnetic particles. Permanent
20 magnets and methods of making permanent magnets described herein are generally directed to encapsulated rare-earth magnetic nanoparticles, particularly encapsulated Nd₂Fe₁₄B nanoparticles, but it is understood that, in some embodiments, other encapsulated magnetic nanoparticles can be used, such as encapsulated metallic magnetic nanoparticles.

[0108] Generally, a permanent magnet comprises a material, the material comprising a
25 plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer or a residue thereof (that is, the material remaining from the protective layer after the formation of the permanent magnet from the plurality of encapsulated nanoparticles). In some embodiments, a permanent magnet is formed by bonding together the material, the material comprising a plurality of
30 encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a

magnetic nanoparticle core encapsulated by a protective layer. In some embodiments, the material further comprises a plurality of additional particles, such as micron-sized particles.

[0109] In some embodiments, the permanent magnet or the material further comprises a plurality of additional particles. In some embodiments, the additional particles are micron-sized particles. In some embodiments, the additional particles are about 100 microns in diameter or less, about 50 microns in diameter or less, about 30 microns in diameter or less, about 20 microns in diameter or less, about 15 microns in diameter or less, about 10 microns in diameter or less, about 5 microns in diameter or less, or about 3 microns in diameter or less. In some embodiments, the additional particles are about 250 nm to about 50 microns, about 500 nm to about 30 microns, or about 1 micron to about 20 microns. In some embodiments, the additional particles are encapsulated particles (that is, particles encapsulated by a protective layer or a residue thereof), for example particles encapsulated by methods similar to the encapsulation of the magnetic nanoparticles as described herein. In some embodiments, the additional particles are not encapsulated by a protective layer. In some embodiments, the additional particles are magnetic particles. In some embodiments, the additional particles are hard magnetic particles. In some embodiments, the additional particles are soft magnetic particles.

[0110] In some embodiments, encapsulated magnetic nanoparticles (such as encapsulated $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles) are used to form an exchange-spring magnet. An exchange spring magnet comprises a hard magnetic component, with a relatively high coercivity, and a soft magnetic component, with a relatively high saturation magnetization. In an exchange spring magnet, the hard magnetic component and the soft magnetic component are combined to produce a composite magnetic material with a high coercivity and high saturation magnetization. Preferably, the hard magnetic component and soft magnetic component comprise magnetic nanoparticles. In some embodiments, a hard magnetic component comprises encapsulated $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles. In some embodiments, the soft magnetic component comprises iron, an iron alloy (such as iron-cobalt alloy, iron-silicon alloy, or nickel-iron alloy), or a ceramic material (such as iron oxide). Additional soft magnetic components are known in the art.

[0111] In some embodiments, the permanent magnet is less than about 50 wt% hard magnetic components, less than about 30 wt% hard magnetic components, less than about 20 wt% hard magnetic components, less than about 15 wt% hard magnetic components, or less than about 10 wt% hard magnetic components. In some embodiments the composite magnetic material is less

than about 30 wt% rare earth metal, less than about 20 wt% rare earth metal, less than about 10 wt% rare earth metal, or less than about 5 wt% rare earth metal.

[0112] In some embodiments, the permanent magnet is formed by bonding together a material, the material comprising encapsulated magnetic nanoparticles. In some embodiments, the material further comprises additional particles, such as micron-sized particles, which may be magnetic or nonmagnetic, or encapsulated or unencapsulated. In some embodiments, the additional particles are hard magnets. In some embodiments, the additional particles are soft magnets. In some embodiments, bonding occurs by pressing (for example, cold pressing) or sintering (for example, spark-plasma sintering). In some embodiments, both pressing and sintering of the material is used to bond the material together. In some embodiments, bonding the material together comprises cold-pressing the material. In some embodiment, bonding the material together comprises sintering the material. In some embodiments, bonding material comprises both cold pressing the material and sintering the material.

[0113] In some embodiments, the permanent magnet is formed by cold pressing the material comprising the plurality of encapsulated magnetic nanoparticles. For example, in some embodiment the nanoparticles are pressed by placing the nanoparticles into a mold and pressing with a compacting force. In some embodiments, an external magnetic field is applied to the nanoparticles before, during, or before and during the pressing process. In some embodiments, the external magnetic field aligns the magnetic particles. In some embodiments, magnetic particles align along a crystal axis of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ material. In some embodiments, the magnetic field is applied parallel to the compacting force (axial pressing). In some embodiments, the magnetic field is applied perpendicular to the compacting force (transverse pressing). In some embodiments, the compacting force is applied in multiple directions (isostatic pressing).

[0114] In some embodiments, the material is sintered together. In some embodiments, the material is sintered together using spark-plasma sintering. Spark-plasma sintering generally preserves the particle size throughout the sintering process, thereby retaining the magnetic properties of the particles. In some embodiment of spark-plasma sintering, a DC current is passed through the magnetic particles to generate an internal heat, which softens the particles, followed by rapid cooling of the particles. Using this process of spark-plasma sintering, the nanoparticles are bonded together without significantly altering the size of the particles. In some

embodiments, the sintering process is performed in an inert or reducing environment, such as in argon gas, in nitrogen gas, in a mixture of hydrogen gas and argon gas, or in a mixture of hydrogen gas and nitrogen gas.

[0115] In some embodiments, about 99% of magnetic particles in the composite magnet have an average diameter or average grain size after being bonded together (for example, by sintering) of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, about 98% of the magnetic particles in the composite magnet have an average diameter or average grain size after being bonded together (for example, by sintering) of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, about 95% of $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles in the composite magnet have an average diameter or average grain size after being bonded together (for example, by sintering) of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, about 90% of $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles in the composite magnet have an average diameter or average grain size after being bonded together (for example, by sintering) of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm. In some embodiments, about 80% of $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles in the composite magnet have an average diameter or average grain size after being bonded together (for example, by sintering) of about 0.5 nm to about 100 nm, or about 1 nm to about 50 nm, or about 1 nm to about 30 nm, or about 1 nm to about 10 nm, or about 2 nm to about 20 nm, or about 2 nm to about 10 nm, or about 2 nm to about 5 nm, or about 2 nm to about 4 nm.

[0116] In some embodiments, the composite magnetic material includes magnetic nanoparticles encapsulated by a silane-derivative protective layer or residue thereof. In some embodiments, as a result of a processing step, such as by bonding the nanoparticles together (for example, by pressing or sintering the particles), the silane-derivative protective layer reacts to form a silane-derivative protective layer residues. In some embodiments, the silane-derivative

protective layer residue includes residual carbon or silicon atoms. In some embodiments, the silane-derivative protective layer is located within spaces separating the magnetic nanoparticle cores.

[0117] In some embodiments, the formed composite magnetic material is machined or molded into a desired shape. In some embodiments, the composite magnetic materials are employed in generators or turbines, such as a permanent magnet synchronous generator, steam turbines, gas turbines, wind turbines, hydro turbines, or reciprocating engines. In some embodiments, the composite magnetic materials are employed in motors. In some embodiments, composite magnetic materials are employed in magnetic resonance imaging systems or other spectroscopy techniques including, but not limited to, nuclear magnetic resonance (NMR) spectroscopy, magnetic probes (for example in bioimaging or therapeutic applications including, but not limited to, contrast agents or localized drug delivery systems).

EXAMPLES

15 *Example 1: Formation of Nd₂Fe₁₄B nanoparticles*

[0118] Micron-sized particles containing approximately 26.2% neodymium, 70.4% iron, 1.79% niobium, and 1.19% boron, by weight excluding oxygen as measured by inductively coupled plasma emission spectroscopy, were fed into a plasma reactor system. X-ray diffraction data suggested the micron-sized particles were Nd₂Fe₁₄B, and no niobium compounds were conclusively observed. A working gas mixture of argon and hydrogen was used in the plasma reactor system, which vaporized the micron-sized particles and produced nano-sized particles of about 3 nm to about 5 nm, as observed by transmission electron microscopy (TEM). The Nd₂Fe₁₄B nanoparticles were collected from the plasma reactor system and stored under argon.

[0119] The Nd₂Fe₁₄B nanoparticles contained approximately 25.4% neodymium, 72.71% iron, 1.01% niobium, and 0.62% boron, by weight excluding oxygen as measured by inductively coupled plasma emission spectroscopy. Similar to the micron-sized particles, X-ray diffraction data suggested the nanoparticles were Nd₂Fe₁₄B, and no niobium compounds were conclusively observed.

Example 2: Encapsulation of Nd₂Fe₁₄B nanoparticles

[0120] Nd₂Fe₁₄B nanoparticles, such as those produced in Example 1, were encapsulated by a silane derivative to protect the nanoparticles from oxidation. 130 grams of Nd₂Fe₁₄B nanoparticles (0.12 moles of Nd₂Fe₁₄B) were suspended in 800 mL methanol and sonicated to produce a dispersion. The dispersion was centrifuged to precipitate any larger agglomerated nanoparticles, and the supernatant comprising nano-sized Nd₂Fe₁₄B nanoparticles was retained.

[0121] Sodium hydroxide (0.4 grams, 0.1 moles) was added to the nanoparticle-methanol dispersion to a final concentration of about 0.05%. Sodium borohydride (4.6 grams, 0.12 moles NaBH₄) was then added to the dispersion at a 1:1 molar ratio of sodium borohydride to Nd₂Fe₁₄B. Dichloromethyl octylsilane (DCMOS) (55 grams, 0.24 moles) was then added to the dispersion at about 2:1 molar ratio of DCMOS to Nd₂Fe₁₄B, and the dispersion was allowed to react for about 30 minutes while mixing at room temperature.

[0122] The reacted dispersion was then centrifuged at a high speed, allowing the encapsulated Nd₂Fe₁₄B nanoparticles to settle. The resulting supernatant was discarded, and the settled Nd₂Fe₁₄B nanoparticles were washed by resuspending the nanoparticles in methanol and allowed to mix for 5 minutes at room temperature. Again the dispersion was centrifuged at a high rate, precipitating the Nd₂Fe₁₄B nanoparticles, and the supernatant was discarded. This washing cycle was repeated, followed by drying the nanoparticles at about 30 °C. The resulting encapsulated nanoparticles were subjected to X-ray photoelectron spectroscopy, and significant metallic Nd₂Fe₁₄B material was observed.

Example 3: Encapsulation of Nd₂Fe₁₄B nanoparticles

[0123] Nd₂Fe₁₄B nanoparticles, such as those produced in Example 1, were encapsulated by a phosphorylation reagent to protect the nanoparticles from oxidation. 130 grams of Nd₂Fe₁₄B nanoparticles (0.12 moles of Nd₂Fe₁₄B) were suspended in 800 mL methanol and sonicated to produce a dispersion. The dispersion was centrifuged to precipitate any larger agglomerated nanoparticles, and the supernatant comprising nano-sized Nd₂Fe₁₄B nanoparticles was retained.

[0124] Sodium hydroxide (0.4 grams, 0.1 moles) was added to the nanoparticle-methanol dispersion to a final concentration of about 0.05%. Sodium borohydride (4.6 grams, 0.12 moles NaBH₄) was then added to the dispersion at a 1:1 molar ratio of sodium borohydride to Nd₂Fe₁₄B. Phosphoric acid (H₃PO₄) (23.5 grams, 0.24 moles) was then added to the dispersion

at about 2:1 molar ratio of H_3PO_4 to $Nd_2Fe_{14}B$, and the dispersion was allowed to react for about 30 minutes while mixing at room temperature.

[0125] The reacted dispersion was then centrifuged at a high speed, allowing the encapsulated $Nd_2Fe_{14}B$ nanoparticles to settle. The resulting supernatant was discarded, and the settled
5 $Nd_2Fe_{14}B$ nanoparticles were washed by resuspending the nanoparticles in methanol and allowed to mix for 5 minutes at room temperature. Again the dispersion was centrifuged at a high rate, precipitating the $Nd_2Fe_{14}B$ nanoparticles, and the supernatant was discarded. This washing cycle was repeated, followed by drying the nanoparticles at about 30 °C. The resulting encapsulated nanoparticles were subjected to X-ray photoelectron spectroscopy, and significant metallic
10 $Nd_2Fe_{14}B$ material was observed.

Example 4: Nanocomposite Magnetic Material

[0126] Encapsulated $Nd_2Fe_{14}B$ nanoparticles, for example those produced in Example 2, are poured into a mold and cold pressed together. An external magnetic field is applied to the
15 pressed particles during the cold pressing process. The particles are then sintered together. An additional magnetic pulse is applied following the sintering process to align the magnetic field. The coercivity, remanence, and energy product of the composite magnetic is then measured.

Example 5: Nanocomposite Exchange Spring Magnet

20 [0127] Encapsulated $Nd_2Fe_{14}B$ nanoparticles, for example those produced in Example 2, are mixed with soft magnetic nanoparticles, poured into a mold, and cold pressed together. An external magnetic field is applied to the cold pressed particles during the pressing process. The particles are then sintered together. An additional magnetic pulse is applied following the sintering process to align the magnetic field. The coercivity, remanence, and energy product of
25 the composite magnetic is then measured.

[0128] The disclosures of all publications, patents, patent applications, and published patent applications referred to herein by an identifying citation are hereby incorporated herein by reference in their entirety.

[0129] The present invention has been described in terms of specific embodiments
30 incorporating details to facilitate the understanding of principles of construction and operation of the invention. Such reference herein to specific embodiments and details thereof is not intended

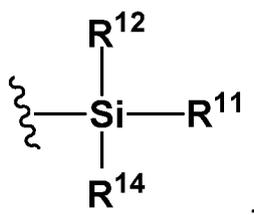
to limit the scope of the claims appended hereto. It will be readily apparent to one skilled in the art that other various modifications can be made in the embodiments chosen for illustration without departing from the spirit and scope of the invention. Therefore, the description and examples should not be construed as limiting the scope of the invention.

CLAIMS

We claim:

1. An encapsulated magnetic nanoparticle comprising a magnetic nanoparticle core encapsulated by a protective layer.
2. The encapsulated magnetic nanoparticle according to claim 1, wherein the protective layer comprises a silane derivative.
3. The encapsulated magnetic nanoparticle according to claim 1, wherein the protective layer comprises phosphate.
4. The encapsulated magnetic nanoparticle according to any one of claims 1-3, wherein the magnetic nanoparticle core is a rare-earth magnetic nanoparticle core.
5. The encapsulated magnetic nanoparticle according to any one of claims 1-4, wherein the magnetic nanoparticle core comprises neodymium, iron, and boron.
6. The encapsulated magnetic nanoparticle according to any one of claims 1-5, wherein the magnetic nanoparticle core comprises a magnetic metal, a magnetic alloy, a magnetic metal alloy, carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium.
7. The encapsulated magnetic nanoparticle according to any one of claims 1-6, wherein the magnetic nanoparticle core comprises niobium.
8. The encapsulated magnetic nanoparticle according to any one of claims 1-7, wherein the magnetic nanoparticle core is plasma generated.
9. The encapsulated magnetic nanoparticle according to any one of claims 1-8, wherein the magnetic nanoparticle core is not produced by ball milling.

10. The encapsulated magnetic nanoparticle according to any one of claims 1-9, wherein the magnetic nanoparticle core has a diameter of about 0.5 nm to about 100 nm.
11. The encapsulated magnetic nanoparticle according to any one of claims 1-10, wherein the magnetic nanoparticle core has a diameter of about 3 nm to about 5 nm.
12. The encapsulated magnetic nanoparticle according to any one of claims 2, and 4-11, wherein the silane derivative is a hydrophobic silane derivative.
13. The encapsulated magnetic nanoparticle according to any one of claims 2, and 4-12, wherein the silane derivative has the formula:



wherein R¹¹ is a hydrophobic group; and

R¹² and R¹⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo.

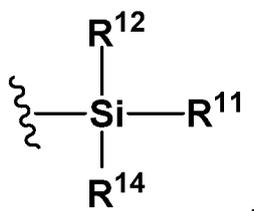
14. The encapsulated magnetic nanoparticle according to claim 13, wherein R¹¹ is -C₂-C₈ alkyl or -C₃-C₁₈ n-alkyl.
15. The encapsulated magnetic nanoparticle according to claim 13 or 14, wherein R¹¹ is selected from -C₆-C₁₈ alkyl.
16. The encapsulated magnetic nanoparticle according to any one of claims 13-15, wherein R¹² and R¹⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro.
17. The encapsulated magnetic nanoparticle according to any one of claims 2, and 4-16, wherein the silane derivative is dimethyl octylsilane or chloromethyl octylsilane.

18. The encapsulated magnetic nanoparticle according to any one of claims 1-17, wherein the protective layer is about 5 nm thick or less.
19. The encapsulated magnetic nanoparticle according to any one of claims 1-18, wherein the protective layer is about 2 nm thick or less.
20. The encapsulated magnetic nanoparticle according to any one of claims 1-19, wherein the protective layer is about 1 nm thick or less.
21. A permanent magnet comprising a material comprising a plurality of the encapsulated magnetic nanoparticles according to any one of claims 1-20.
22. The permanent magnet according to claim 21, wherein the material further comprises a plurality of micron-sized particles.
23. The permanent magnet according to claim 22, wherein the micron-sized particles comprise magnetic micron-sized particles.
24. The permanent magnet according to claim 22 or 23, wherein the micron-sized particles comprise encapsulated micron-sized particles.
25. The permanent magnet according to any one of claims 22-24, wherein the micron-sized particles comprise unencapsulated micron-sized particles.
26. The permanent magnet according to any one of claims 21-25, wherein the material is bonded together.
27. The permanent magnet according to any one of claims 21-26, wherein the material is cold pressed together.

28. The permanent magnet according to claim 26 or 27, wherein an external magnetic field is applied to the material while the material is bonded or cold pressed together.
29. The permanent magnet according to any one of claims 21-28, wherein the material is sintered together.
30. The permanent magnet according to claim 29, wherein the material is spark-plasma sintered together.
31. The permanent magnet according to any one of claims 21-30, wherein the material comprises a soft magnetic component.
32. A motor comprising a permanent magnet according to any one of claims 21-31.
33. A generator comprising a permanent magnet according to any one of claims 21-32.
34. A permanent magnet comprising a material, the material comprising a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer or a residue thereof.
35. The permanent magnet according to claim 34, wherein the material further comprises a plurality of micron-sized particles.
36. The permanent magnet according to claim 35, wherein the micron-sized particles comprise magnetic micron-sized particles.
37. The permanent magnet according to claim 35 or 36, wherein the micron-sized particles comprise encapsulated micron-sized particles.

38. The permanent magnet according to any one of claims 35-37, wherein the micron-sized particles comprise unencapsulated micron-sized particles.
39. The permanent magnet according to any one of claims 34-38, wherein the protective layer comprises a silane derivative.
40. The permanent magnet according to any one of claims 34-38, wherein the protective layer comprises phosphate.
41. The permanent magnet according to any one of claims 34-40, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are rare-earth magnetic nanoparticle cores.
42. The permanent magnet according to any one of claims 34-41, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles comprise neodymium, iron, and boron.
43. The permanent magnet according to any one of claims 34-42, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles comprise a magnetic metal, a magnetic alloy, a magnetic metal alloy, carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium.
44. The permanent magnet according to any one of claims 34-43, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles comprise niobium.
45. The permanent magnet according to any one of claims 34-44, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are plasma generated.

46. The permanent magnet according to any one of claims 34-45, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are not produced by ball milling.
47. The permanent magnet according to any one of claims 34-46, wherein about 80% or more of the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm.
48. The permanent magnet according to any one of claims 34-47, wherein about 80% or more the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles have a diameter of about 3 nm to about 5 nm.
49. The permanent magnet according to any one of claims 34-39 and 41-48, wherein the silane derivative is a hydrophobic silane derivative.
50. The permanent magnet according to any one of claims 34-39 and 41-49, wherein the silane derivative has the formula:



wherein R^{11} is a hydrophobic group; and

R^{12} and R^{14} are independently selected from the group consisting of $-\text{C}_4$ alkyl, $-\text{OC}_4$ alkyl, halo, chloro, bromo, and iodo.

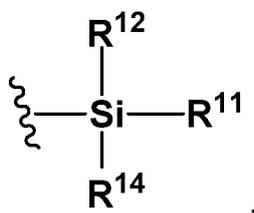
51. The permanent magnet according to claim 50, wherein R^{11} is C_2 - C_8 alkyl or $-\text{C}_3$ - C_{18} n-alkyl.
52. The permanent magnet according to claim 50 or 51, wherein R^{11} is selected from $-\text{C}_6$ - C_{18} alkyl.

53. The permanent magnet according to any one of claims 50-52, wherein R¹² and R¹⁴ are independently selected from the group consisting -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro.
54. The permanent magnet according to any one of claims 34-39, and 41-53, wherein the silane derivative is dimethyl octylsilane or chloromethyl octylsilane.
55. The permanent magnet according to any one of claims 34-54, wherein the protective layer is about 5 nm thick or less.
56. The permanent magnet according to any one of claims 34-55, wherein the protective layer is about 2 nm thick or less.
57. The permanent magnet according to any one of claims 34-56, wherein the protective layer is about 1 nm thick or less.
58. The permanent magnet according to any one of claims 34-57, wherein the permanent magnet is molded or machined into a desired shape.
59. The permanent magnet according to any one of claims 34-58, wherein the permanent magnet is used in a generator or turbine.
60. The permanent magnet according to any one of claims 34-59, wherein the permanent magnet is used in a motor.
61. A permanent magnet formed by bonding together a material comprising a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer.
62. The permanent magnet according to claim 61, wherein the material further comprises a plurality of micron-sized particles.

63. The permanent magnet according to claim 62, wherein the plurality of micron-sized particles is combined with the plurality of encapsulated magnetic nanoparticles prior to bonding together the plurality of encapsulated magnetic nanoparticles.
64. The permanent magnet according to claim 62 or 63, wherein the micron-sized particles comprise magnetic micron-sized particles.
65. The permanent magnet according to any one of claims 62-64, wherein the micron-sized particles comprise encapsulated micron-sized particles
66. The permanent magnet according to any one of claims 62-65, wherein the micron-sized particles comprise unencapsulated micron-sized particles.
67. The permanent magnet according to any one of claims 61-66, wherein the protective layer comprises a silane derivative.
68. The permanent magnet according to any one of claims 61-66, wherein the protective layer comprises phosphate.
69. The permanent magnet according to any one of claims 61-68, wherein the material is cold-pressed together.
70. The permanent magnet according to any one of claims 61-69, wherein an external magnetic field is applied to the material while the material is bonded together.
71. The permanent magnet according to any one of claims 61-70, wherein the material is sintered together.
72. The permanent magnet according to claim 71, wherein the material is spark-plasma sintered together.

73. The permanent magnet according to any one of claims 61-72, wherein the magnetic nanoparticle core is a rare-earth magnetic nanoparticle core.
74. The permanent magnet according to any one of claims 61-73, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles comprises neodymium, iron, and boron.
75. The permanent magnet according to any one of claims 61-74, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles comprise a magnetic metal, a magnetic alloy, a magnetic metal alloy, carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium.
76. The permanent magnet according any one of claims 61-75, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles comprise niobium.
77. The permanent magnet according any one of claims 61-76, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are plasma generated.
78. The permanent magnet according any one of claims 61-77, wherein the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles are not produced by ball milling.
79. The permanent magnet according to any one of claims 61-78, wherein 80% or more of the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm.

80. The permanent magnet according to any one of claims 61-79, wherein 80% or more the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles have a diameter of about 3 nm to about 5 nm.
81. The permanent magnet according to any one of claims 61-67 and 69-80, wherein the silane derivative is a hydrophobic silane derivative.
82. The permanent magnet according to any one of claims 61-67 and 69-81, wherein the silane derivative has the formula:



wherein R¹¹ is a hydrophobic group; and

R¹² and R¹⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OCi-C₄ alkyl, halo, chloro, bromo, and iodo.

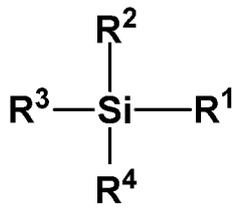
83. The permanent magnet according to claim 82, wherein R¹¹ is -C₂-C₈ alkyl or -C₃-C₁₈ n-alkyl.
84. The permanent magnet according to claim 82 or 83, wherein R¹¹ is selected from -C₆-C₁₈ alkyl.
85. The permanent magnet according to any one of claims 82-84, wherein R¹² and R¹⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro.
86. The permanent magnet according to any one of claims 61-67 and 69-85, wherein the silane derivative is dimethyl octylsilane or chloromethyl octylsilane.

87. The permanent magnet according to any one of claims 61-86, wherein the protective layer is about 5 nm thick or less.
88. The permanent magnet according to any one of claims 61-87, wherein the protective layer is about 2 nm thick or less.
89. The permanent magnet according to any one of claims 61-88, wherein the protective layer is about 1 nm thick or less.
90. The permanent magnet according to any one of claims 61-89, wherein the material comprises soft magnetic component.
91. A motor comprising a permanent magnet according to any one of claims 61-90.
92. A generator comprising a permanent magnet according to any one of claims 61-90.
93. A method of making encapsulated magnetic nanoparticles comprising:
 - suspending a plurality of magnetic nanoparticles in an inert solvent to form a dispersion;
 - combining the dispersion with sodium borohydride; and
 - combining the dispersion with a protective-layer reagent.
94. The method of making encapsulated magnetic nanoparticles according to claim 93, wherein the protective-layer reagent is a silanization reagent.
95. The method of making encapsulated magnetic nanoparticles according to claim 93, wherein the protective-layer reagent is a phosphorylation reagent.
96. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-95, wherein the inert solvent is an alcohol.

97. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-96, wherein the inert solvent is methanol or isopropanol.
98. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-97, further comprising nano-sizing a plurality of micron-sized magnetic particles to form the plurality of magnetic nanoparticles.
99. The method of making encapsulated magnetic nanoparticles according to claim 98, wherein the nano-sizing step is performed using plasma.
100. The method of making encapsulated magnetic nanoparticles according to claim 98 or 99, wherein the nano-sizing step is not performed by ball milling.
101. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-100, wherein the plurality of magnetic nanoparticles has an average diameter of about 30 nm or less.
102. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-101, wherein the plurality of magnetic nanoparticles has an average diameter of about 20 nm or less.
103. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-102, wherein the plurality of magnetic nanoparticles has an average diameter of about 10 nm or less.
104. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-103, wherein the plurality of magnetic nanoparticles has an average diameter of about 5 nm or less.

105. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-104, wherein 80% or more of the magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm.
106. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-105, wherein 80% or more the magnetic nanoparticles have a diameter of about 3 nm to about 5 nm.
107. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-106, further comprising washing the encapsulated magnetic nanoparticles.
108. The method of making encapsulated magnetic nanoparticles according to claim 107, wherein the washing step occurs in an inert solvent.
109. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-108, further comprising centrifuging the dispersion.
110. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-109, further comprising sonicating the dispersion.
111. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-110, further comprising combining sodium hydroxide with the dispersion.
112. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-111, further comprising drying the encapsulated magnetic nanoparticles.
113. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-112, wherein the magnetic nanoparticles are rare-earth magnetic nanoparticles.

114. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-113, wherein the magnetic nanoparticles comprise neodymium, iron, and boron.
115. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-114, wherein the magnetic nanoparticles comprise a magnetic metal, a magnetic alloy, a magnetic metal alloy, carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium.
116. The method of making encapsulated magnetic nanoparticles according to any one of claims 93-115, wherein the magnetic nanoparticles comprise niobium.
117. The method of making encapsulated magnetic nanoparticles according to any one of claims 94 and 96-116, wherein the silanization reagent is a hydrophobic silanization reagent.
118. The method of making encapsulated magnetic nanoparticles according to any one of claims 94 and 96-117, wherein the silanization reagent has the formula:



wherein R¹ is a hydrophobic group; R² and R⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo; and R³ is a leaving group.

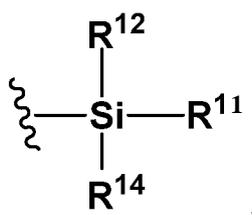
119. The method of making encapsulated magnetic nanoparticles according to claim 118, wherein R¹ is -C₂-C₁₈ alkyl or -C₃-C₁₈ n-alkyl.
120. The method of making encapsulated magnetic nanoparticles according to claim 118 or 119, wherein R¹ is selected from -C₆-C₁₈ alkyl.

121. The method of making encapsulated magnetic nanoparticles according to any one of claims 118-120, wherein R^2 and R^4 are independently selected from the group consisting of $-CH_3$, $-CH_2CH_3$, $-OCH_3$, $-OCH_2CH_3$, and chloro.
122. The method of making encapsulated magnetic nanoparticles according to any one of claims 118-121, wherein R^3 is selected from the group consisting of iodo, bromo, chloro, or sulfonate.
123. The method of making encapsulated magnetic nanoparticles according to any one of claims 94 and 96-122, wherein the silanization reagent is dimethylchloro octylsilane or dichloromethyl octylsilane.
124. The method of making encapsulated magnetic nanoparticles according to any one of claims 95-116, wherein the phosphorylation reagent is phosphoric acid.
125. A method of making a permanent magnet comprising bonding together a material comprising a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer.
126. The method of making a permanent magnet according to claim 125, the material further comprising a plurality of micron-sized particles.
127. The method of making a permanent magnet according to claim 126, wherein the micron-sized particles comprise magnetic micron-sized particles.
128. The method of making a permanent magnet according to claim 126 or 127, wherein the micron-sized particles comprise encapsulated micron-sized particles.
129. The method of making a permanent magnet according to any one of claims 126-128, wherein the micron-sized particles comprise unencapsulated micron-sized particles.

130. The method of making a permanent magnet according to any one of claims 125-129, wherein the protective layer comprises a silane derivative.
131. The method of making a permanent magnet according to any one of claims 125-129, wherein the protective layer comprises phosphate.
132. The method of making a permanent magnet according to any one of claims 125-131, comprising cold pressing the material.
133. The method of making a permanent magnet according to any one of claims 125-132, wherein an external magnetic field is applied during the bonding step or the cold pressing step.
134. The method of making a permanent magnet according to any one of claims 125-133, comprising sintering the material.
135. The method of making a permanent magnet according to claim 134, comprising spark-plasma sintering the material.
136. The method of making a permanent magnet according to any one of claims 125-135, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles are rare-earth magnetic nanoparticle cores.
137. The method of making a permanent magnet according to any one of claims 125-136, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise neodymium, iron, and boron.
138. The method of making a permanent magnet according to any one of claims 125-137, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles

comprise a magnetic metal, a magnetic alloy, a magnetic metal alloy, carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium.

139. The method of making a permanent magnet according to any one of claims 125-138, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise niobium.
140. The method of making a permanent magnet according to any one of claims 125-139, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles are plasma generated.
141. The method of making a permanent magnet according to any one of claim 125-140, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles are not produced by ball milling.
142. The method of making a permanent magnet according to any one of claims 125-141, wherein 80% or more of the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm.
143. The method of making a permanent magnet according to any one of claims 125-142, wherein 80% or more of the magnetic nanoparticle cores of the plurality of encapsulated magnetic nanoparticles have a diameter of about 3 nm to about 5 nm.
144. The method of making a permanent magnet according to any one of claims 130 and 132-143, wherein the silane derivative is a hydrophobic silane derivative.
145. The method of making a permanent magnet according to any one of claims 130 and 132-144, wherein the silane derivative has the formula:



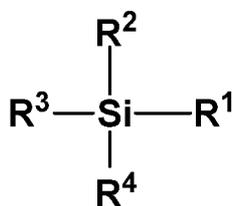
wherein R¹¹ is a hydrophobic group; and

R¹² and R¹⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OCi-C₄ alkyl, halo, chloro, bromo, and iodo.

146. The method of making a permanent magnet according to claim 145, wherein R¹¹ is -C₂-C₈ alkyl or -C₃-C₈ n-alkyl.
147. The method of making a permanent magnet according to claim 145 or 146, wherein R¹¹ is selected from -C₆-C₁₈ alkyl.
148. The method of making a permanent magnet according to any one of claims 145-147, wherein R¹² and R¹⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro.
149. The method of making a permanent magnet according to any one of claims 130 and 132-148, wherein the silane derivative is dimethyl octylsilane or chloromethyl octylsilane.
150. The method of making a permanent magnet according to any one of claims 131-143, wherein the phosphate is derived from phosphoric acid.
151. The method of making a permanent magnet according to any one of claims 125-150, wherein the protective layer is about 5 nm thick or less.
152. The method of making a permanent magnet according to any one of claims 125-151, wherein the protective layer is about 2 nm thick or less.

153. The method of making a permanent magnet according to any one of claims 125-152, wherein the protective layer is about 1 nm thick or less.
154. The method of making a permanent magnet according to any one of claims 125-153, wherein the plurality of encapsulated magnetic nanoparticles is formed by:
 - suspending a plurality of magnetic nanoparticles in an inert solvent to form a dispersion;
 - combining the dispersion with sodium borohydride; and
 - combining the dispersion with a protective-layer reagent.
155. The method of making a permanent magnet according to claim 154, wherein the protective-layer reagent is a silanization reagent.
156. The method of making a permanent magnet according to claim 154, wherein the protective-layer reagent is a phosphorylation reagent.
157. The method of making a permanent magnet according to any one of claims 154-156, wherein the inert solvent is an alcohol.
158. The method of making a permanent magnet according to any one of claims 154-157, wherein the inert solvent is methanol or isopropanol.
159. The method of making a permanent magnet according to any one of claims 154-158, further comprising nano-sizing a plurality of micron-sized magnetic particles to form the plurality of magnetic nanoparticles.
160. The method of making a permanent magnet according to claim 159, wherein the nano-sizing step is performed using plasma.
161. The method of making a permanent magnet according to claim 159 or 160, wherein the nano-sizing step is not performed by ball milling.

162. The method of making a permanent magnet according to any one of claims 154-161, further comprising washing the encapsulated magnetic nanoparticles.
163. The method of making a permanent magnet according to claim 162, wherein the washing step occurs in an inert solvent.
164. The method of making a permanent magnet according to any one of claims 154-163, further comprising centrifuging the dispersion.
165. The method of making a permanent magnet according to any one of claims 154-164, further comprising sonicating the dispersion.
166. The method of making a permanent magnet according to any one of claims 154-165, further comprising combining sodium hydroxide with the dispersion.
167. The method of making a permanent magnet according to any one of claims 154-166, further comprising drying the encapsulated magnetic nanoparticles.
168. The method of making a permanent magnet according to any one of claims 155 and 157-167, wherein the silanization reagent is a hydrophobic silanization reagent.
169. The method of making a permanent magnet according to any one of claims 155 and 157-168, wherein the silanization reagent has the formula:

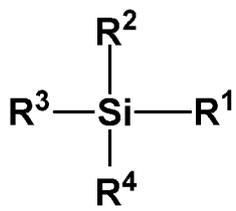


wherein R^1 is a hydrophobic group; R^2 and R^4 are independently selected from the group consisting of $-\text{Ci}-\text{C}_4$ alkyl, $-\text{OCi}-\text{C}_4$ alkyl, halo, chloro, bromo, and iodo; and R^3 is a leaving group.

170. The method of making a permanent magnet according to claim 169, wherein R^1 is $-C_2-C_{18}$ alkyl or $-C_3-C_{18}$ n-alkyl.
171. The method of making a permanent magnet according to claim 169 or 170, wherein R^1 is selected from $-C_6-C_{18}$ alkyl.
172. The method of making a permanent magnet according to any one of claims 169-171, wherein R^2 and R^4 are independently selected from the group consisting of $-CH_3$, $-CH_2CH_3$, $-OCH_3$, $-OCH_2CH_3$, and chloro.
173. The method of making a permanent magnet according to any one of claims 169-172, wherein R^3 is selected from the group consisting of iodo, bromo, chloro, or sulfonate.
174. The method of making a permanent magnet according to any one of claims 155 and 157-173, wherein the silane derivative is dimethylchloro octylsilane or dichloromethyl octylsilane.
175. The method of making a permanent magnet according to any one of claims 156-167, wherein the phosphorylation reagent is phosphoric acid.
176. The method of making a permanent magnet according to any one of claims 125-175, the material further comprising a plurality of soft magnetic particles.
177. A method of making a permanent magnet comprising:
forming a material comprising a plurality of encapsulated magnetic nanoparticles, the encapsulated magnetic nanoparticles comprising a magnetic nanoparticle core encapsulated by a protective layer; and
bonding the material together.

178. The method of making a permanent magnet according to claim 177, wherein forming the material comprises:
- suspending a plurality of magnetic nanoparticles in an inert solvent to form a dispersion;
 - combining the dispersion with sodium borohydride; and
 - combining the dispersion with a protective-layer reagent, thereby forming the plurality of encapsulated magnetic nanoparticles.
179. The method of making a permanent magnet according to claim 178, further comprising nano-sizing a plurality of micron-sized magnetic particles to form the plurality of magnetic nanoparticles.
180. The method of making a permanent magnet according to claim 179, wherein the nano-sizing step is performed using plasma.
181. The method of making a permanent magnet according to claim 179 or 180, wherein the nano-sizing step is not performed by ball milling.
182. The method of making a permanent magnet according to any one of claims 178-181, wherein the inert solvent is an alcohol.
183. The method of making a permanent magnet according to any one of claims 178-182, wherein the inert solvent is methanol or isopropanol.
184. The method of making a permanent magnet according to any one of claims 178-183, further comprising sonicating the dispersion.
185. The method of making a permanent magnet according to any one of claims 178-184, further comprising centrifuging the dispersion.

186. The method of making a permanent magnet according to any one of claims 178-185, further comprising combining sodium hydroxide into the dispersion.
187. The method of making a permanent magnet according to any one of claims 178-186, wherein the protective-layer reagent is a silanization reagent.
188. The method of making a permanent magnet according to claim 187, wherein the silanization reagent is a hydrophobic silanization reagent.
189. The method of making a permanent magnet according to claim 187 or 188, wherein the silanization reagent has the formula:



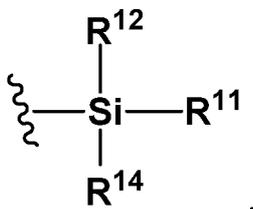
wherein R¹ is a hydrophobic group; R² and R⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo; and R³ is a leaving group.

190. The method of making a permanent magnet according to claim 189, wherein R¹ is -C₂-C₈ alkyl or -C₃-C₁₈ n-alkyl.
191. The method of making a permanent magnet according to claim 189 or 190, wherein R¹ is selected from -C₆-C₁₈ alkyl.
192. The method of making a permanent magnet according to any one of claims 189-191, wherein R² and R⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro.
193. The method of making a permanent magnet according to any one of claims 189-192, wherein R³ is selected from the group consisting of iodo, bromo, chloro, or sulfonate.

194. The method of making a permanent magnet according to any one of claims 189-193, wherein the silanization reagent is dimethylchloro octylsilane or dichloromethyl octylsilane.
195. The method of making a permanent magnet according to any one of claims 178-186, wherein the protective-layer reagent is a phosphorylation reagent.
196. The method of making a permanent magnet according to any one of claims 195, wherein the phosphorylation reagent is phosphoric acid.
197. The method of making a permanent magnet according to any one of claims 178-196, further comprising washing the encapsulated magnetic nanoparticles.
198. The method of making a permanent magnet according to claim 197, wherein the washing step occurs in an inert solvent.
199. The method of making a permanent magnet according to any one of claims 178-198, further comprising drying the encapsulated magnetic nanoparticles.
200. The method of making a permanent magnet according to any one of claims 177-199, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 30 nm or less.
201. The method of making a permanent magnet according to any one of claims 177-200, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 20 nm or less.
202. The method of making a permanent magnet according to any one of claims 177-201, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 10 nm or less.

203. The method of making a permanent magnet according to any one of claims 177-202, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have an average diameter of about 5 nm or less.
204. The method of making a permanent magnet according to any one of claims 177-203, wherein 80% or more of the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have a diameter of about 0.5 nm to about 100 nm.
205. The method of making a permanent magnet according to any one of claims 177-204, wherein 80% or more of the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles have a diameter of about 3 nm to about 5 nm.
206. The method of making a permanent magnet according to any one of claims 177-205, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles are rare-earth magnetic nanoparticle cores.
207. The method of making a permanent magnet according to any one of claims 177-206, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise neodymium, iron, and boron.
208. The method of making a permanent magnet according to any one of claims 177-207, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise a magnetic metal, a magnetic alloy, a magnetic metal alloy, carbon, cobalt, copper, dysprosium, gallium, niobium, zinc, or zirconium.
209. The method of making a permanent magnet according to any one of claims 177-208, wherein the magnetic nanoparticle cores of the encapsulated magnetic nanoparticles comprise niobium.

210. The method of making a permanent magnet according to any one of claims 177-209, wherein the protective layer comprises a silane derivative.
211. The method of making a permanent magnet according to claim 210, wherein the silane derivative is a hydrophobic silane derivative.
212. The method of making a permanent magnet according to claim 210 or 211, wherein the silane derivative has the formula:



wherein R¹¹ is a hydrophobic group; and

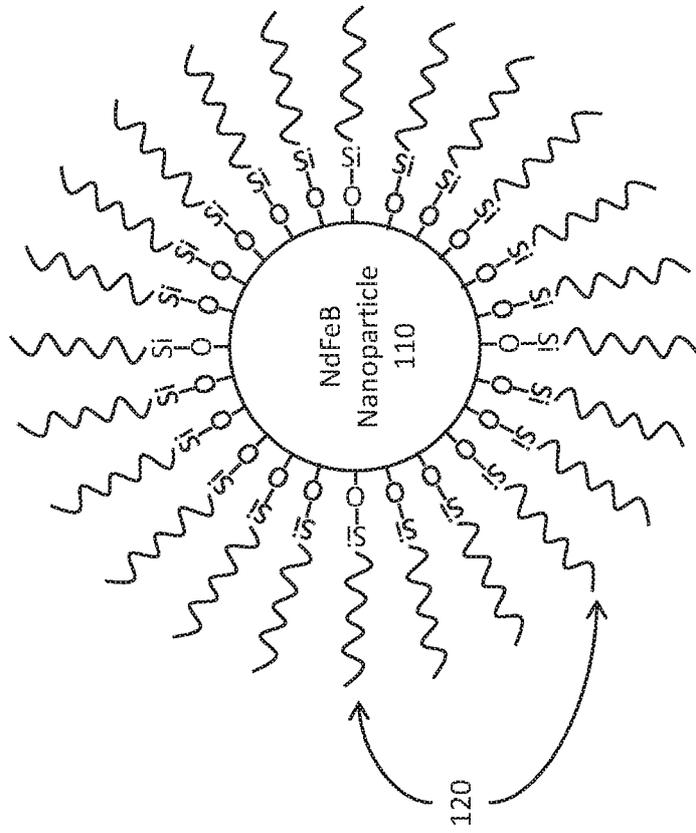
R¹² and R¹⁴ are independently selected from the group consisting of -C₁-C₄ alkyl, -OC₁-C₄ alkyl, halo, chloro, bromo, and iodo.

213. The method of making a permanent magnet according to claim 212, wherein R¹¹ is -C₂-C₈ alkyl or -C₃-C₁₈ n-alkyl.
214. The method of making a permanent magnet according to claim 212 or 213, wherein R¹¹ is selected from -C₆-C₁₈ alkyl.
215. The method of making a permanent magnet according to any one of claims 212-214, wherein R¹² and R¹⁴ are independently selected from the group consisting of -CH₃, -CH₂CH₃, -OCH₃, -OCH₂CH₃, and chloro.
216. The method of making a permanent magnet according to any one of claims 212-215, wherein the silane derivative is dimethyl octylsilane or chloromethyl octylsilane.
217. The method of making a permanent magnet according to any one of claims 177-209, wherein the protective layer comprises phosphate.

218. The method of making a permanent magnet according to any one of claims 177-217, wherein the protective layer is about 5 nm thick or less.
219. The method of making a permanent magnet according to any one of claims 177-218, wherein the protective layer is about 2 nm thick or less.
220. The method of making a permanent magnet according to any one of claims 177-219, wherein the protective layer is about 1 nm thick or less.
221. The method of making a permanent magnet according to any one of claims 177-220, wherein forming the material further comprises combing a plurality of micron-sized particles with the plurality of encapsulated magnetic nanoparticles.
222. The method of making a permanent magnet according to claim 221, wherein the micron-sized particles comprise magnetic micron-sized particles.
223. The method of making a permanent magnet according to claim 221 or 222, wherein the micron-sized particles comprise encapsulated micron-sized particles.
224. The method of making a permanent magnet according to any one of claims 221-223, wherein the micron-sized particles comprise unencapsulated micron-sized particles.
225. The method of making a permanent magnet according to any one of claims 177-224, comprising cold pressing the material.
226. The method of making a permanent magnet according to any one of claims 177-225, wherein an external magnetic field is applied during the bonding step or cold pressing step.

227. The method of making a permanent magnet according to any one of claims 177-226, comprising sintering the material.
228. The method of making a permanent magnet according to claim 227, comprising spark-plasma sintering the material.
229. The method of making a permanent magnet according to any one of claims 177-228, wherein forming the material comprises combining a plurality of soft magnetic particles with the plurality of encapsulated magnetic nanoparticles.
230. A permanent magnet made by a method according to any one of claims 125-229.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/21024

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01F 1/00; H01F 7/02; H01F 1/06; H01F 1/053; H01F 41/00; B82Y 5/00 (2016.01)**CPC** - H01F 1/0045; H01F 1/015; H01F 1/0555; H01F 1/061; H01F 41/026; B82Y 5/00; B82Y 25/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - H01F 1/00; H01F 7/02; H01F 1/06; H01F 1/053; H01F 41/00; B82Y 5/00 (2016.01)

CPC - H01F 1/0045; H01F 1/015; H01F 1/0555; H01F 1/061; H01F 41/026; B82Y 5/00; B82Y 25/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and non-patent literature (classification, keyword; search terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Scholar (NPL), Google Patents; search terms: permanent magnet, encapsulated magnetic nanoparticles, nanoparticle core, rare-earth, encapsulated, protective layer, suspend, dispersion, inert solvent, alcohol, sodium borohydride, silane, phosphate, phosphorylate, bonding together, micron-sized particles, nano-sizing, plasma, ball-mill

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2006/0177879 A1 (MAYES et al.) 10 August 2006 (10.08.2006) para [0001], [0010]-[0011], [0015], [0019], [0021], [0023], [0030]-[0032], [0049]	1-2, 4, 34-37, 61-64, 93-94, 96, 125-128 ----- 95
X --- Y	US 2014/0255502 A1 (CHEN et al.) 11 September 2014 (11.09.2014) para [0002], [0004], [0008], [0027], [0037], [0049]	1, 3 ----- 95
X	Gubin et al., "Magnetic nanoparticles: preparation, structure and properties" Russian Chemical Reviews, Vol. 74, No. 6 (2005) [online] [retrieved on 25 April 2016]. Retrieved from the Internet <URL: http://physicsonline.ru/PaperLogos/7329/files/Full_text_English_version.pdf > entire document, especially pg 490, 491, 493, 495, 499, 502	34, 177-181
A	Shihai He, "Synthesis of Hard Magnetic Nanoparticles for Applications in Permanent Magnets" Diss. Univ. of Minnesota (December 2014) [online] [retrieved on 20 April 2016]. Retrieved from the Internet <URL: http://con3servancy.uinn.edu/bltstream/handle/11299/171126/HE_umn_0130E_1_5630.pdf?sequence=1&isAllowed=y >	34-37, 61-64, 125-128, 177-181
A	US 3,424,578 A (STRNAT et al.) 28 January 1969 (28.01.1969) col 1, ln 14-16, 18-25; col 2, ln 36, 40-42; col 3, ln 18-27, 41-45, 48-54, 62-70	34-37, 61-64, 125-128, 177-181

 Further documents are listed in the continuation of Box C.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
25 April 2016 (25.04.2016)

Date of mailing of the international search report

06 JUN 2016

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-8300Authorized officer:
Lee W. YoungPCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/21024

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014/0374643 A1 (MIO et al.) 25 December 2014 (25.12.2014) para [0003], [0007], [0012]	34-37, 61-64, 125-128, 177-181
A	US 3,933,535 A (BECKER) 20 January 1976 (20.01.1976) col 1, ln 7-8; col 3, ln 15-39, 51-65, 68; col 4, ln 1-4; col 5, ln 1-4; claim 1	34-37, 61-64, 125-128, 177-101
A	US 2010/0283570 A1 (LAVOIE et al.) 11 November 2010 (11.11.2010) entire document	1-, 34-37, 61-64, 93-96, 125-128, 177-181
A	McBain et al., "Magnetic nanoparticles for gene and drug delivery" Int. J. Nanomedicine, Vol. 3, No. 2 (2008) [online] [retrieved on 25 April 2016]. Retrieved from the Internet <URL: http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2527670/pdf/ijn-0302-169.pdf > entire document	1-, 34-37, 61-64, 93-96, 125-128, 177-181

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 16/21024

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 5-33, 38-60, 65-92, 97-124, 129-176, 182-230
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. HI Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.