

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 September 2007 (27.09.2007)

PCT

(10) International Publication Number
WO 2007/109304 A2

(51) International Patent Classification: Not classified

(21) International Application Number:
PCT/US2007/006993

(22) International Filing Date: 20 March 2007 (20.03.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/784,051 20 March 2006 (20.03.2006) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: CERAMIC NANOPARTICLES AND METHODS FOR FORMING CERAMIC NANOPARTICLES FROM ELECTROSPUN NANOFIBERS

(57) Abstract: The subject invention pertains to polycrystalline, ceramic nanofibers and nanoparticles, processes for preparing the nanofibers and nanoparticles, and methods for their use. The subject processes include applying energy to a solution containing electrospun, annealed nanofibers in a solvent. Advantageously, the processes of the subject invention produce uniformly shaped nanoparticles that are useful as insulating layers in, for example, capacitors.



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DESCRIPTION

CERAMIC NANOPARTICLES AND METHODS FOR FORMING CERAMIC
NANOPARTICLES FROM ELECTROSPUN NANOFIBERS

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application Serial No. 60/784,051, filed March 20, 2006, which is hereby incorporated by reference in its entirety, including all figures and tables.

BACKGROUND OF THE INVENTION

Ferroelectric materials can be defined as materials that show net spontaneous polarization without an externally applied field and can be reversed and reoriented with the direction of the externally applied field (Lines *et al.*, 1977; Cardarelli, 2001). Stable ferroelectric polarization can be used to form digital signals such as 1 and 0, and they are the basis of memory and logic circuits (O'Brien *et al.*, 2001). Metal oxides with perovskite structure such as BaTiO₃ and Pb(Zr,Ti)O₃ are widely used in various electronic applications that take advantage of their unique ferroelectric, pyroelectric, and piezoelectric properties. For example, they are widely used for multi-layer ceramic capacitors (MLCC), transducers, actuators and ferroelectric random access memories (FRAM) (Scott, 1998; Mathews *et al.*, 1997; Park *et al.*, 1999).

Over the last few decades, one dimensional nanomaterials such as nanotubes and nanofibers have attracted great attention due to their unique structure and properties such as high aspect ratio, large specific surface area, and chemical/mechanical stabilities. Thus, nanofibers can be used as building blocks in nanotechnology (Dzenis, 2004; Rao *et al.*, 2004). Previously, several ceramic nanowires have been synthesized by various techniques, for example, solution method, laser ablation, and chemical vapor deposition (CVD) (Iijima, 1991; Morales *et al.*, 1998; Martin, 1994; Han *et al.*, 1997). A major disadvantage of these methods is the need of multiple process steps to produce nanowires. Etching and purification processes are good examples of such extra processing steps, which are both time and cost consuming processes (Dzenis, 2004; Li *et al.*, 2003).

Ceramic nanoparticles are currently fabricated using a variety of techniques. Generally, nanoparticles are either fabricated using a "bottom-up" method or a "top down" method. In a bottom-up method, the nanoparticles are synthesized directly to the desired shape and size.

5 One such bottom-up method, electrospray deposition, transforms a liquid into nanosized particles by applying voltage to a capillary containing a solution. When the electrostatic force becomes stronger than the surface tension of the liquid, the solution exits the capillary as a highly charged jet of fluid. Coulomb's Explosion denotes the formation of droplets due to the charge of the jet stream. As the solvent evaporates from the droplets,
10 particles form and are deposited onto a collector. Unfortunately, the electrospraying method requires an expensive collection system.

Another bottom-up method, sol-gel processing, produces particles by a series of hydrolysis and condensation reactions to first form a sol of particles suspended in a liquid phase. The particles can be isolated from the sol by precipitation. The disadvantages of sol-
15 gel processing include the toxic chemicals required for the reactions, the length of the preparation time, and the high cost of production.

An example of a top down technique is a mechanical method like ball milling. Ball milling usually involves using fixed and moving elements to reduce larger particles into micron-sized and nanosized particles. The material to be ground is reduced in size due to the
20 interaction between the fixed elements, the moving elements, and the material itself. Unfortunately, ball milling usually produces nanoparticles that are not uniform in both size and shape. Additionally, ball milling requires an increasing amount of energy and time to produce incrementally smaller sized particles. The mill itself must be able to withstand constant vibration and the heat generated from the friction inherent to its use. A high energy
25 ball mill is utilized in mechanicochemical synthesis to mill at least two different powders until the particles are sufficiently fine so that their surface and strain energies sustain the ceramic producing reaction.

BRIEF SUMMARY OF THE INVENTION

30 The subject invention pertains to uniformly sized and/or shaped ceramic nanoparticles. Nanoparticles within the scope of the present invention include, without limitation, tetragonal barium titanate, titania, $\text{Pb}(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$, and $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$.

The subject invention also concerns processes for preparing ceramic nanofibers and uniformly sized and/or shaped ceramic nanoparticles. In one embodiment, ceramic, electrospun nanofibers are added to a solvent of choice and subjected to an application of energy. If energy is applied by sonication, then the sonication reduces the nanofibers into nanoparticles. The maximum nanoparticle size is confined by the diameter of the nanofiber, which is controlled entirely by the solution and processing parameters of the electrospinning process. Advantageously, this eliminates the need of expensive installations for controlling the size of the particles or for collecting them. Additionally, processes of the subject invention for making ceramic nanoparticles are inexpensive and non-toxic relative to previous techniques, produce nanoparticles with uniform size and shape, and make large quantities of nanoparticles.

A specific embodiment for producing ceramic nanoparticles of the subject invention comprises providing a plurality of electrospun nanofibers composed of a ceramic-polymer composite, calcinating the nanofibers for a sufficient time to crystallize the ceramic nanofibers, dispersing the calcinated nanofibers into a solvent, and applying a sufficient amount of energy to the solution to break apart the nanofibers into nanoparticles.

The present invention also relates to methods for utilizing the nanoparticles of the subject invention. In one embodiment, at least one layer of nanoparticles of the subject invention is applied to at least a portion of a substrate. The subject invention also concerns substrates comprising at least one layer of a nanoparticle of the invention. Exemplary substrates include, without limitation, circuits, capacitors, and crystal silicon wafers.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 illustrates a scanning electron microscopic image of TiO_2 nanofibers before sonication. These nanofibers were electrospun at 15KV with a 5cc syringe that had a 16 gauge 2 in. syringe tip. After electrospinning, the nanofibers were calcinated at 500°C for 3 hours.

Figure 2 illustrates a scanning electron microscopic image of the TiO_2 nanoparticles produced when the TiO_2 nanofibers shown in Figure 1 are sonicated in a deionized water, sonication bath for 15 minutes.

Figure 3 illustrates the size distribution of the TiO_2 nanoparticles shown in Figure 2.

Figure 4 illustrates BaTiO_3 particles synthesized by electrospinning. BaTiO_3 electrospun nanofibers were heat-treated at 750°C for an hour and ultrasonicated by

ultrasonic horn for an hour. The solvent used for particle formation was isopropanol. The parameters of the digital instruments nanoscope that produced this photograph include: scan size, 3.000 μm ; scan rate, 1.650 Hz; number of samples, 512; image data, deflection; data scale, 20:00 nm; engage x Pos, 145084.8 μm ; engage x Pos, 36323.6 μm .

5 **Figure 5A** illustrates a scanning electronic microscopic image of barium titanium and PVP composite nanofibers prior to annealing.

Figure 5B illustrates BaTiO_3 nanofibers annealed at 750°C for one hour.

Figure 5C shows the polycrystalline fiber morphology.

10 **Figure 6A** illustrates X-ray diffraction (XRD) patterns of barium titanate nanofibers dried at 80°C for one hour.

Figure 6B illustrates XRD patterns for barium titanate nanofibers annealed at 650°C for one hour.

Figure 6C illustrates XRD patterns for barium titanate nanofibers annealed at 750°C for one hour.

15 **Figure 7A** illustrates a transmission electron microscopic image of barium titanate nanofibers annealed at 750°C.

Figure 7B illustrates a high resolution image of a barium titanate nanofiber that shows lattice fringes.

20 **Figure 7C** illustrates the convergent beam electron diffraction (CBED) pattern obtained from electrospun barium titanate nanofibers (accelerating voltage: 200 kV; camera length: 12 cm; zone axis [134]).

Figure 8 illustrates the HR-XRD pattern around 45° of 2 θ of a tetragonal barium titanate nanoparticle of the subject invention.

25 **Figure 9** illustrates a peak fitting curve of the HR-XRD pattern of Figure 9. The peak fitting curve reveals the location of peaks (002) and (200).

Figure 10 illustrates the Raman spectra of a tetragonal barium titanate nanoparticle of the subject invention.

DETAILED DISCLOSURE OF THE INVENTION

The subject invention concerns ceramic nanoparticles exhibiting piezoelectric properties and methods for their preparation and use. The nanoparticles of the subject invention are useful as the insulating layers in, for example, capacitors. Inclusion of a layer of nanoparticles can improve capacitor storage by a factor of about 5000.

The nanoparticles of the subject invention are composed of polycrystalline, ceramic materials. Suitable ceramic materials include, without limitation, alumina, titania (TiO_2), zirconia, mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), barium titanate (BaTiO_3), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), celsian ($\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$), barium osumilite ($\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$), SiC, MoSi_2 , MgAl_2O_4 , Mg_2Si_4 , ZrB_2 , B_2O_3 , $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$, $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, NiFe_2O_4 , Fe_3O_4 , $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, MgTiO_3 , NiTiO_3 , $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, CeO_2 , ZrO_2 , Al_2O_3 , GeO_2 , $\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$, Co_3O_4 , Nb_2O_5 , NiO/ZnO , PVP-TiO_2 , La_2CuO_4 , SiO_2 , or B_4C . Preferably, the subject nanoparticles are composed of titania, barium titanate, $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$, or $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$.

The nanoparticles of the subject invention are equiaxial in structure. An equiaxed structure, or in this instance, an equiaxed nanoparticle, is an irregular shape between a cube and a sphere, and it has substantially the same dimensions in the three coordinate directions. Moreover, it is solid and compact having no pores or bubbles enclosed within the structure.

Although the size of the nanoparticles are determined by the diameters of the nanofibers used to make the nanoparticles, in one embodiment, the equivalent structure diameter of any one subject nanoparticle may be any diameter within the range from about 10 nm to about 500 nm. Advantageously, since the diameter of the precursor nanofibers determines the diameter of the nanoparticles, the size of the nanoparticles may be tailored to any size diameter by varying the process conditions used to prepare the nanofiber. Numerous conditions and techniques for electrospinning ceramic nanofibers are known in the art and include those disclosed in Sigmund *et al.* 2006, which is hereby incorporated by reference in its entirety.

In one embodiment, the nanoparticle diameter is within the range of about 10 nm to about 300 nm. In another embodiment, the diameters are within the range of about 10 nm to about 130 nm. The diameters are within the range of about 10 nm to about 50 nm in one embodiment and within the range of about 10 nm to about 20 nm in a second embodiment. Exemplary diameters of the subject nanoparticles include, for example, about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24

nm, about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm.

5 In a specific embodiment, the nanoparticles are titania nanoparticles. Although it is not ferroelectric, titania nanoparticles advantageously exhibit properties that are suitable in various applications, for example and without limitation, sunscreen, wall paint, superhydrophilic surfaces (for example, self cleaning windows), and photocatalysts in the destruction of chemicals and biological particles (*e.g.*, viruses, bacteria, fungi, and spores).
10 Furthermore, the titania nanoparticles of the subject invention are potentially useful as a candidate to replace SiO₂ as a gate dielectric capacitor in semiconductors because its rutile phase has a high dielectric constant.

In one embodiment, the subject nanoparticles are Pb(Zr,Ti)O₃ nanoparticles. Advantageously, these nanoparticles exhibit piezoelectric behavior.

15 One specific embodiment of the subject invention pertains to tetragonal barium titanate nanoparticles. Barium titanate nanoparticles exhibit piezoelectric behavior. Surprisingly, the barium titanate nanoparticles, which are less than 500 nm in diameter, exhibit piezoelectric behavior despite their small size. This novel property derives from the electric field and electric charge found in the electrospun nanofibers that are subsequently
20 processed into the subject nanoparticles. The tetragonal perovskite structure is inherently ferroelectric. Thus, the tetragonal nanoparticles of the subject invention are also ferroelectric, thereby having both pyroelectric and piezoelectric properties.

Figures 8 and 9 illustrate the structural characterization of the tetragonal structure of barium titanate of the subject invention. In the R-XRD patterns, the separation of (200) peak to (200) and (002) peaks indicates that the structure is tetragonal. In contrast, the cubic
25 barium titanate usually only shows as a single peak.

The location of the peaks of Figures 8 and 9 is also disclosed in Table 1.

Table 1

JCPDS card (2 θ)	Barium Titanate fibers (2 θ)	Error (2 θ)
44.855	44.877	0.022
45.377	45.266	-0.111

Figure 10 illustrates the Raman spectra for electrospun barium titanate fibers. Raman lines are seen at 305 and 720 wave numbers. Raman modes of 306, 515, and 715 cm^{-1} are characteristic of tetragonal barium titanate. These are assigned only to tetragonal barium titanate and do not appear in the previously known cubic structure of barium titanate.

5 Table 2 provides a comparison of the reported tetragonal Raman spectra for barium titanate and the barium titanate used in the subject invention.

Table 2

Reported tetragonal Raman spectra (cm^{-1}) of BaTiO_3	Barium Titanate fibers Raman spectra (cm^{-1})	Error (cm^{-1})
303 - 306	306	0
515 - 516	515	0 - 1
715 - 721	715	0

10 Another aspect of the subject invention pertains to methods for synthesizing the subject nanoparticles. The methods comprise electrospinning a ceramic-polymer composite nanofiber, annealing the nanofiber, adding the annealed nanofiber to a solvent, and applying energy to the nanofiber in solution to reduce the nanofiber into nanoparticles. In one embodiment, the method comprises electrospinning a plurality of nanofibers.

15 Any electrospinning technique can be used to prepare the nanofibers. Generally, in electrospinning of ceramic nanofibers, conventional sol-gel precursors are mixed with a polymer solution that is ejected from a capillary. When voltage is applied, the formed droplet is deformed due to the influence of the electric field. The droplet of the precursor mixture changes from a spherical to a conical shape. When the electric field overcomes the surface
 20 tension of the precursor droplet, jet emission begins and travels down to the counter electrode. The stability of the jet arises from extensional viscosity of the polymer solution and the presence of entanglement of the polymer in solution. In addition, the viscosity of the polymer prevents the jets from transforming into liquid droplets.

Since electrospinning of ceramics is based on polymer solutions containing ceramic
 25 precursors, theories for electrospinning of polymers can be applied with modifications accounting for the increased electrical conductivity as well as solids loading (solids $\rightarrow$ ceramic precursors) and viscosity as described in Sigmund *et al.*, 2006, which is herein incorporated by reference. Further details and description of suitable polymer

electrospinning processes can be found elsewhere (Shin *et al.*, 2001a; Shin *et al.*, 2001b; Reneker *et al.*, 1996; Reneker *et al.*, 2000). Concerning ceramics, several binary and ternary electrospun nanofibers have been synthesized such as titania (Li *et al.*, 2003), germanium dioxide (Viswanathamuthi *et al.*, 2004), nickel ferrite (Li *et al.*, 2003) and Pt coated silicon substrate supported PZT (Wang *et al.*, 2004).

As noted herein, the diameters of the electrospun nanofibers determine the maximum diameter of the nanoparticles of the subject invention. Thus, the diameters of the nanofibers may be adjusted via the electrospinning process and modifications thereto, thereby adjusting the sizes of any nanoparticles produced by the processes of the subject invention.

In a specific embodiment, the electrospun nanofibers have diameters in the range of between about 10 nm to about 600 nm. In another specific embodiment, the diameters are within the range of about 20 nm to about 360 nm.

Advantageously, the electrospinning technique takes place within a high electrical field (~1-2 kV/cm). Accordingly, the electrospinning technique induces a charge in the resulting nanofiber system. Moreover, the electrospun nanofibers exhibit no crystallinity. They are amorphous composites of the ceramic material and a volatile organic polymer.

Another electrospinning technique relates to electrospinning a nanoparticle in suspension. Herein, the resulting nanofibers exhibit the same crystallinity of the nanoparticles of the subject invention.

The step of annealing the amorphous, electrospun nanofibers comprises subjecting the nanofibers to a heat treatment, whereby a polycrystalline, ceramic nanofiber is produced. This polycrystalline, ceramic nanofiber comprises a plurality of grains held together by van der Waal forces and possibly particle necking. The step of annealing the nanofibers burns off the volatile organic polymer and crystallizes the remaining non-volatile components into ceramic nanofibers. Advantageously, the annealing time and amount of heat applied to the nanofibers can be varied to produce the desired nanoparticle diameter. A less severe heat treatment results in the subsequent production of smaller nanoparticle diameters. Likewise, more severe heat treatments result in nanoparticle diameters that approach those of the nanofibers themselves. Thus, the conditions under which the methods of the subject invention are performed may be adjusted to arrive at the desired nanoparticle diameter. Also, in another embodiment, the methods of the subject invention are performed at numerous conditions to prepare a range of nanoparticle diameters.

The annealed nanofiber diameter is smaller than the diameter of the electrospun nanofibers and in one embodiment, is within the range of about 10 nm to about 190 nm. In one embodiment, the diameter of the annealed nanofibers is within the range of about 10 nm to about 170 nm. In another embodiment, the annealed nanofiber diameter is within about 10 nm to about 150 nm. In a specific embodiment, the diameter of the annealed nanofiber is within about 10 nm to about 140 nm.

Advantageously, the length of the annealed nanofiber is determined by electrospinning techniques and conditions. Thus, the nanofibers utilized in the subject invention may exceed about 10 nm in length. In one embodiment, the length of the nanofiber is within the range of about 10 nm to about 1 m, including about 10 nm to about 1 mm, about 1 mm to about 1 cm, or about 1 cm to about 1 m. Nanofibers whose lengths exceed about 1 m are contemplated by the methods of the subject invention. For example, in yet another embodiment, the length of the annealed nanofiber is from about 1 m to about 10 m. In another embodiment, the length of the annealed nanofiber is greater than about 10 m.

In one embodiment, the nanofibers are heated to and maintained at a temperature within the range of about 400°C to about 800°C. All individual temperatures within the range are contemplated within the scope of the invention. For example, the temperature may be about 400 °C, about 450 °C, about 500 °C, about 550 °C, about 600 °C, about 650 °C, about 700 °C, about 750 °C, or about 800 °C. Other exemplary ranges of temperatures include, without limitation, from about 400 °C to about 600 °C, from about 600 °C to about 800 °C, and from about 500 °C to about 700 °C. The temperature varies for different materials and for creating different sized grains. As noted above, the severity of the heat treatment impacts the size of the grains.

In one embodiment, the time period to which the nanofibers are subjected to the heat treatment varies from about 0.5 hours to about three hours. In yet another specific embodiment, the heat treatment is sustained from about 1 hour to about 2 hours. In some instances, the nanofibers are annealed at 750°C for about 1 hour. In yet another embodiment, the nanofibers are annealed at 650°C for about 1 hour. In yet a third specific embodiment, the nanofibers are annealed at about 500°C for about 2 hours. However, the skilled artisan can determine suitable combinations of annealing temperature and time period to prepare the anneal nanofibers of the subject invention.

The continuous polycrystalline nanofiber produced by the subject methods is composed of a plurality of grains or segments held together by particle-particle interactions

(that is, van der Waals forces). The grains are generally within about 25 nm to about 50 nm in size. However, the invention also contemplates grain size at about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm.

Nanofibers of the present invention include, for example, those made from alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), barium titanate (BaTiO_3), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), celsian ($\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$), barium osumilite ($\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$), SiC, MoSi_2 , MgAl_2O_4 , Mg_2Si_4 , ZrB_2 , B_2O_3 , $\text{Pb}(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$, $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, NiFe_2O_4 , Fe_3O_4 , $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, MgTiO_3 , NiTiO_3 , Al_2O_3 - B_2O_3 , CeO_2 , ZrO_2 , Al_2O_3 , GeO_2 , Mn_2O_3 - Mn_3O_4 , Co_3O_4 , Nb_2O_5 , NiO/ZnO , PVP- TiO_2 , La_2CuO_4 , SiO_2 , or B_4C . In one embodiment, the nanofibers are composed of titania, barium titanate, $\text{Pb}(\text{Zr}, \text{Sn}, \text{Ti})\text{O}_3$, or $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$.

The step of adding the annealed nanofibers to a solvent comprises contacting the annealed nanofibers with a solvent. Optionally, contacting also comprises mixing the annealed nanofibers so that they are dispersed homogenously throughout the solution. Generally, the nanofibers of barium titanate disperse well in water or organic solvents. In another embodiment, the nanofibers in solution aggregate together.

Solvents utilized by the subject invention include any organic solvent or deionized (DI) water. Exemplary organic solvents include, without limitation, hexane, benzene, toluene, diethyl ether, chloroform, ethyl acetate, tetrahydrofuran (THF), methylene chloride, acetone, acetonitrile (MeCN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetic acid, *n*-butanol isopropanol, *n*-propanol, ethanol, methanol, formic acid, carbon tetrachloride, trichloroethylene 2-ethoxyethanol, 2-methoxyethanol, methyl chloride *n*-hexane, tetrachloroethylene, acrylamide, carbon disulfide, ethylene oxide, hydrogen sulfide, methane, methyl mercaptan, methyl-*n*-butyl ketone (MBK), methylene chloride (dichloromethane), organochlorine, organophosphates, perchlorethylene, styrene, 1,1,1-trichloroethane (methyl chloroform), trichloroethylene, vinyl chloride, and xylene. Preferably, the solvent is isopropanol or DI water.

The step of applying energy to the nanofiber solution advantageously reduces the annealed nanofibers to nanoparticles and includes many techniques known in the art. Surprisingly, the annealed nanofibers do not disperse throughout the solvent when the energy is applied. Instead, the forces holding together the nanofiber grains are broken resulting in a

plurality of nanoparticles in solution. Advantageously, the resulting nanoparticles in solution are dispersed and generally are not agglomerated or aggregated.

Preferably, a mechanical application (for example, ball milling, standard milling, attrition milling, knife milling, or rotor milling) or sonication is utilized to reduce the nanofibers to nanoparticles. Although the subject methods contemplate various mechanical applications for preparing the nanoparticles, ball milling is described for the purposes of illustration. Ball milling the nanofiber solution pertains to contacting the nanofiber solution with at least one grinding element, wherein the solution and the grinding element are housed in a vessel. The interaction between the at least one grinding element, the inner surface of the vessel, and the nanofibers breaks the nanofibers into individual nanoparticles due to friction, centrifugal forces, and Coriolis forces. This interaction, advantageously, reduces the nanofibers into nanoparticles because the van der Waal forces and any necking holding the nanoparticles, or grains, to one another are broken. The ball milling occurs for a sufficient amount of time and speed to reduce the nanofibers into discrete nanoparticles. Preferably, the nanofiber solution is ground for about 1 hour at a speed of about 90 rpm. However, the skilled artisan can determine appropriate combinations of speed and grinding time to reduce the annealed nanofibers into nanoparticles.

Typically, the at least one grinding element is in the shape of a sphere; however, other suitably shaped grinding elements are contemplated by the methods of the subject invention. In one embodiment, the subject methods utilize only one grinding element. In yet another embodiment, the methods of the subject invention use two grinding elements. In another embodiment, three or more grinding elements are placed within the milling vessel. The diameter of the at least one grinding ball is preferably about 3 mm. Additionally, the grinding element is free to move within the vessel in ball milling.

The vessel is composed of materials that are resistant to wear and tear and sample contamination. Suitable materials include, without limitation, stainless steel, agate, tungsten carbide, and ceramics. Preferably, the vessel is prepared from yttrium-stabilized zirconium oxide (YSZ). Optionally, the vessel may be fitted with a stainless steel protective jacket to protect the vessel from shattering if dropped or subjected to other similar impact forces.

Removal of each grinding element requires separation of the nanoparticles from the element itself. One technique involves passing the contents of the ball milling vessel through a sieve whose openings are bigger than the diameter of the nanoparticles. The nanoparticles and solution pass through the sieve, and each grinding element is collected in the sieve screen.

Any collected grinding elements can be subsequently washed to remove any residual nanoparticles.

Alternately, the contents of the vessel can be dried to remove the solvent, and the dried nanoparticle-grinding element mixture can be placed on a three-dimensional sieve shaker. The nanoparticles pass through the sieve screen because of the vibrations induced by the shaker.

Sonication of the nanofiber solution can be provided by many sonication techniques known in the art. Sonication generally relates to creating high frequency mechanical vibrations by stimulating crystals with high frequency oscillating electrical currents. Exemplary sonication techniques include both sonication bath and sonication horn. The preferred frequency of the acoustic waves varies from about 20,000 Hz to about 23,000 Hz. In one embodiment, the nanofiber solution is sonicated in a bath for about 15 minutes. In yet another embodiment, the nanofiber solution is sonicated by ultrasonic horn for about an hour.

Advantageously, any type of sonication and sonicating equipment can apply the sufficient amount of energy to reduce the electrospun nanofibers to nanoparticles. Generally, a longer period of sonicating at higher frequency promotes the formation of nanoparticles from nanofibers. However, the skilled artisan can determine suitable combinations of sonication time and frequency to prepare the subject nanoparticles. Although the preferred particle size is about 100 nm or less, larger particles made from multiple grains can be prepared by optimizing the sonication process.

The subject methods optionally include the step of collecting the nanoparticles. The step of collecting includes methods for separating the nanoparticles from the solution and includes, for example and without limitation, filtering, sieving, volatilizing the solvent, and the like.

Another aspect of the present invention relates to methods for utilizing the nanoparticles of the subject invention. Specifically, the subject methods are directed to applying at least one layer of the subject nanoparticles to a substrate. In one embodiment, the subject methods apply only one layer of nanoparticles to the substrate. In yet another embodiment, the subject methods apply two layers of nanoparticles to the substrate. In another specific embodiment, the subject methods apply three or more layers of nanoparticles to the substrate. The methods of the subject invention also contemplate multiple layers wherein the nanoparticle layer is surrounded on the top and/or below with a layer other than a nanoparticle layer. The thickness of the nanoparticle layer can be as thin as the diameter of

the subject nanoparticles or as thick as necessary to insulate the underlying substrate. Exemplary substrates include, without limitation, circuits, capacitors, and crystal silicon wafers.

As used herein, the terms “sonication,” “ultrasonic mixing,” and “ultrasonication” are interchangeable and all refer to the technique that uses the application of acoustic energy.

As used herein, the terms “anneal,” “annealing,” “calcination,” “calcinate,” and “calcinating” are interchangeable and all refer to the technique wherein the electrospun, amorphous nanofibers are subjected to a heat treatment.

The terms “comprising,” “consisting of,” and “consisting essentially of” are defined according to their standard meaning and may be substituted for one another throughout the instant application in order to attach the specific meaning associated with each term.

As used in this specification and the appended claims, the singular forms “a,” “an,” and “the” include plural reference unless the context clearly dictates otherwise. Thus, for example, a reference to “a nanofiber” includes more than one such nanofiber and a references to “the nanoparticles” includes a single nanoparticle and the like.

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

Following is an example that illustrates procedures for practicing the invention. These examples should not be construed as limiting. All percentages are by weight, and all solvent mixture proportions are by volume unless otherwise noted.

EXAMPLE -- Preparation of BaTiO₃ nanoparticles

Barium titanate nanofibers with perovskite structure were synthesized by electrospinning. Sol-gel precursors were utilized along with high molecular weight polymers yielding electrospun nanofibers that were dried and annealed. Polycrystalline barium titanate fibers were obtained after annealing at 750 °C for 1 hour. Typical fiber morphology was 80–190 nm in diameter and over 0.1 mm in length.

Ternary perovskite oxide nanofibers via the electrospinning process and nanoparticles were investigated. The BaTiO₃ nanofibers were prepared as follows. Based on conventional sol-gel processes, barium acetate and titanium isopropoxide were used as starting materials. To achieve stoichiometric BaTiO₃, 1:1 molar ratio was maintained. First, 1.275 g of

Ba(CH₃COO)₂ was dissolved in 3 ml of acetic acid and stirred for 2 hours. Then, 1.475 ml of [(CH₃)₂CHO]₄Ti was added drop by drop under continuous stirring (Kozuka *et al.*, 2001). After dissolution of all compounds, the precursor solution was mixed with a solution consisting of poly(vinyl pyrrolidone) (PVP, M_w=1,300,000) dissolved in ethanol (PVP: 0.2 g and ethanol: 3 ml). After being stirred at room temperature for 2 hours, the mixture was loaded into a plastic syringe. A positive terminal was connected to the syringe needle tip while aluminum foil covered collector worked as counter electrode. A non-woven mat structure of BaTiO₃ nanofibers was synthesized by applying 15 kV to the solution through the needle tip. The distance between the syringe needle tip and the collector was fixed at 7 cm. The as-synthesized mat of composite nanofibers was dried in a vacuum oven at 80 °C for an hour. The dried mat of nanofibers was annealed at different temperatures, 650 °C and 750 °C, for 60 min each.

Studies of morphologies and dimensions of the nanofibers were conducted by field emission scanning electron microscopy (SEM) operating at 15 kV (JSM-6335F, JEOL, Peabody, USA). Powder X-ray patterns were obtained to investigate phases and crystal structures of both annealed and as-synthesized nanofibers (APD 3720, Philips, New York, USA). Transmission electron microscopy operating at 200 kV (J-2010F, JEOL, Peabody, USA) was utilized to further analyze the microstructure and crystal structure of the nanofibers. The SEM images of electrospun barium titanate fibers are shown in Figures 5A and 5B. It can be seen in Figure 5A that the surface of dried composite fibers is smoother due to the amorphous nature of barium titanate PVP composite.

Table 3. Average and Standard Deviation of Fiber Diameters: As-Synthesized and Annealed Fibers at 750°C

	Average fiber diameter (nm)	Standard deviation (nm)
As-synthesized fibers	273	57
Fibers annealed at 750°C	116	30

Diameters of at least 25 fibers were measured for both as-synthesized and annealed fibers. Diameters of as-synthesized fibers vary from 180 to 360 nm. After annealing at 750 °C for an hour, the PVP is fully decomposed, and a polycrystalline fiber is obtained. Due to PVP burn out, the average diameter was reduced by about 60% (Table 3). However, even though the diameters of the electrospun nanofibers were reduced (Figure 5B), their

continuous microstructure was maintained. The inset in Figure 5B shows that the fibers were made up of grains between 25 nm and 50 nm in size with typical fiber diameter between 80 nm and 190 nm. Typical length of the annealed fibers was in the order of a few hundred micrometers up to millimeters.

5 X-ray diffraction (XRD) patterns of barium titanate nanofibers annealed at different conditions are shown in Figures 6A-6C. The XRD pattern of as-synthesized and dried composite samples as shown in Figure 6A indicated an amorphous state of the nanofibers. After annealing at 650 °C (Figure 6B), onset of BaTiO₃ perovskite crystallization is evident although non-perovskite peaks ($\sim 27^\circ - 2\theta$) and amorphous background still remains. Figure
10 6C, an XRD pattern of nanofibers annealed at 750 °C, shows well-defined perovskite peaks with higher intensity and no detectable secondary phases.

Transmission electron microscope (TEM) images of BaTiO₃ nanofiber collected after annealing are presented in Figures 7A, 7B, and 7C. The bright field TEM image indicated that the fibers consisted of barium titanate grains of approximately 25–50 nm. High
15 resolution TEM of an individual grain sticking out of the fiber (as indicated by the arrow in Figure 7A) showed the lattice fringes confirming the crystallinity of the individual grains (Figure 7B). The selected area electron diffraction pattern (SAEDP) of the individual grain from the BaTiO₃ nanofiber is presented in Figure 7C. Indexing of the SAEDP is consistent [134] type zone axis for a tetragonal perovskite and was confirmed through crystallographic
20 simulations.

This unusual zone axis is the result of the limited tilting conditions imposed by fiber morphology. Orientation of the individual grain is limited as additional tilting results in diffraction patterns collected from more than one grain. However, the SAEPD is a further confirmation of the crystallinity of the fibers.

25 Furthermore, since the crystallographic analysis of the nanofibers confirmed a tetragonal perovskite crystal structure, ferroelectricity can be expected.

The BaTiO₃ nanofibers that were annealed at 750°C for one hour were further processed into nanoparticles. The nanofibers were placed into solution with isopropanol and ultrasonicated by an ultrasonic horn for one hour. The uniformity of the resulting
30 nanoparticles is illustrated in Figure 4. The diameters of the nanoparticles are no larger than about 100 nm under these synthesis conditions. The phase of the nanoparticles is tetragonal perovskite. This is confirmed by HR-XRD and Raman spectroscopy as illustrated in Figures 8, 9, and 10.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

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CLAIMS

We claim:

- 5 1. A method of preparing a nanoparticle, said method comprising:
- a) obtaining a ceramic-polymer composite nanofiber;
 - b) annealing said ceramic-polymer composite nanofiber;
 - c) contacting said annealed nanofiber with a solvent; and
 - d) applying energy to said annealed nanofiber, whereby said nanofiber is reduced to a
- 10 nanoparticle.
2. The method according to claim 1, wherein said nanofiber is obtained by electrospinning a ceramic-polymer composite nanofiber from a solution.
- 15 3. The method according to claim 2, wherein said nanofiber is dried following said electrospinning.
4. The method according to claim 1, wherein said nanofiber comprises one or more of alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), barium titanate
- 20 (BaTiO_3), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), celsian ($\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$), barium osumilite ($\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$), SiC, MoSi₂, MgAl_2O_4 , Mg_2Si_4 , ZrB_2 , B_2O_3 , $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$, $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, NiFe_2O_4 , Fe_3O_4 , $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, MgTiO_3 , NiTiO_3 , $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, CeO_2 , ZrO_2 , Al_2O_3 , GeO_2 , $\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$, Co_3O_4 , Nb_2O_5 , NiO/ZnO , PVP- TiO_2 , La_2CuO_4 , SiO_2 , or B_4C .
- 25 5. The method according to claim 1, wherein said ceramic-polymer composite nanofiber has a diameter of about 10 nm to about 600 nm.
6. The method according to claim 1, wherein said ceramic-polymer composite nanofiber has a diameter of about 20 nm to about 360 nm.
- 30 7. The method according to claim 1, wherein said annealing in step (b) comprises heating said ceramic-polymer composite nanofiber.

8. The method according to claim 7, wherein said ceramic-polymer composite nanofiber is heated at a temperature from about 400 °C to about 800 °C.

5 9. The method according to claim 7, wherein said ceramic-polymer composite nanofiber is heated at a temperature of about 400 °C; or about 450 °C; or about 500 °C; or about 550 °C; or about 600 °C; or about 650 °C; or about 700 °C; or about 750 °C; or about 800 °C

10 10. The method according to claim 7, wherein said ceramic-polymer composite nanofiber is heated at a temperature from about 400 °C to about 600 °C.

11. The method according to claim 7, wherein said ceramic-polymer composite nanofiber is heated at a temperature from about 600 °C to about 800 °C.

15 12. The method according to claim 7, wherein said ceramic-polymer composite nanofiber is heated at a temperature from about 500 °C to about 700 °C.

20 13. The method according to claim 1, wherein said annealed nanofiber has a diameter of about 10 nm to about 190 nm.

14. The method according to claim 1, wherein said annealed nanofiber has a diameter of about 10 nm to about 170 nm.

25 15. The method according to claim 1, wherein said annealed nanofiber has a diameter of about 10 nm to about 150 nm.

16. The method according to claim 1, wherein said annealed nanofiber has a diameter of about 10 nm to about 140 nm.

30 17. The method according to claim 1, wherein said annealed nanofiber has a length of about 10 nm to more than 10 m.

18. The method according to claim 1, wherein said annealed nanofiber has a length of about 10 nm to about 1 m.

19. The method according to claim 1, wherein said annealed nanofiber has a length of
5 about 10 nm to about 1 mm.

20. The method according to claim 1, wherein said annealed nanofiber has a length of about 1 mm to about 1 cm.

10 21. The method according to claim 1, wherein said annealed nanofiber has a length of about 1 cm to about 1 m.

22. The method according to claim 1, wherein said annealed nanofiber is composed of a plurality of grains or segments, wherein said grains or segments are about 25 nm, about
15 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm in diameter.

20 23. The method according to claim 7, wherein said ceramic-polymer composite nanofiber is heated for about 0.5 hours to about 3 hours.

24. The method according to claim 7, wherein said ceramic-polymer composite nanofiber is heated at about 650 °C to about 750 °C for about 1 hour; or at about 500 °C for
25 about 2 hours.

25. The method according to claim 1, wherein said solvent is water or an organic solvent.

30 26. The method according to claim 25, wherein said organic solvent is selected from the group consisting of hexane, benzene, toluene, diethyl ether, chloroform, ethyl acetate, tetrahydrofuran (THF), methylene chloride, acetone, acetonitrile (MeCN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetic acid, *n*-butanol, isopropanol,

n-propanol, ethanol, methanol, formic acid, carbon tetrachloride, trichloroethylene 2-ethoxyethanol, 2-methoxyethanol, methyl chloride *n*-hexane, tetrachloroethylene, acrylamide, carbon disulfide, ethylene oxide, hydrogen sulfide, methane, methyl mercaptan, methyl-*n*-butyl ketone (MBK), methylene chloride (dichloromethane), organochlorine,
5 organophosphates, perchlorethylene, styrene, 1,1,1-trichloroethane (methyl chloroform), trichloroethylene, vinyl chloride, and xylene.

27. The method according to claim 25, wherein said solvent is isopropanol.

10 28. The method according to claim 25, wherein said solvent is deionized water.

29. The method according to claim 1, wherein step (c) further comprises mixing said annealed nanofiber in said solvent.

15 30. The method according to claim 1, wherein said energy in step (d) is provided by mechanical or sonic means.

31. The method according to claim 30, wherein said mechanical means is provided by ball milling, standard milling, attrition milling, knife milling, or rotor milling.

20 32. The method according to claim 31, wherein said milling comprises at least one grinding element.

25 33. The method according to claim 30, wherein said sonic means comprises high frequency sound waves.

34. The method according to claim 33, wherein said sound waves have a frequency of about 20,000Hz to about 23,000 Hz.

30 35. The method according to claim 1, wherein said nanofiber is electrospun from a polymer solution comprising ceramic precursor compounds.

36. The method according to claim 35, wherein said polymer solution comprises poly(vinyl pyrrolidone).

37. The method according to claim 35, wherein said ceramic precursor compounds
5 are barium acetate and titanium isopropoxide.

38. The method according to claim 7, wherein said ceramic-polymer composite fiber is heated for a period of time and at a temperature sufficient to burn off the polymer from said ceramic-polymer composite nanofiber.

39. The method according to claim 1, wherein conditions for said annealing step are selected to produce nanoparticles having a range of diameters.

40. The method according to claim 1, wherein said nanoparticle is collected.

41. The method according to claim 40, wherein said nanoparticle is collected by filtering, sieving, or volatilization.

42. The method according to claim 1, wherein said nanoparticle has a diameter of
20 about 10 nm to about 500 nm.

43. The method according to claim 1, wherein said nanoparticle has a diameter of about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about
25 23 nm, about 24 nm, about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm.

44. A nanoparticle comprising a ceramic compound.

45. The nanoparticle according to claim 44, wherein said nanoparticle comprises alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), barium titanate (BaTiO_3), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), celsian ($\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$), barium osumilite ($\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$), SiC, MoSi₂, MgAl_2O_4 , Mg_2Si_4 , ZrB_2 , B_2O_3 , $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$, $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$,
5 NiFe_2O_4 , Fe_3O_4 , $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, MgTiO_3 , NiTiO_3 , $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, CeO_2 , ZrO_2 , Al_2O_3 , GeO_2 , $\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$, Co_3O_4 , Nb_2O_5 , NiO/ZnO , PVP- TiO_2 , La_2CuO_4 , SiO_2 , or B_4C .

46. The nanoparticle according to claim 45, wherein said nanoparticle comprises barium titanate and said nanoparticle is tetragonal in structure.

47. The nanoparticle according to claim 44, wherein said nanoparticle is equiaxial in structure

48. The nanoparticle according to claim 44, wherein said nanoparticle has a diameter
15 of about 10 nm to about 500 nm.

49. The nanoparticle according to claim 44, wherein said nanoparticle has a diameter of about 10 nm, 11 nm, 12 nm, 13 nm, 14 nm, 15 nm, 16 nm, 17 nm, 18 nm, 19 nm, 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24 nm, about 25 nm, about 26 nm, about 27
20 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm.

50. The nanoparticle according to claim 44, wherein said nanoparticle comprises $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$.

51. The nanoparticle according to claim 44, wherein said nanoparticle comprises titania (TiO_2).

52. A nanoparticle produced by the method of any of claims 1 to 43.

53. A nanofiber comprising a ceramic-polymer composite.

54. A substrate comprising at least one layer of a nanoparticle according to any of claims 44 to 52.

5 55. The substrate according to claim 54, wherein said substrate is a circuit, a capacitor, or a silicon wafer.

56. A composition comprising a nanoparticle according to any of claims 44 to 52.

10 57. The composition according to claim 56, wherein said composition comprises a mixture of nanoparticles having different ceramic compounds, wherein said ceramic compounds are selected from the group consisting of alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), barium titanate (BaTiO_3), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), celsian ($\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$), barium osumilite ($\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$), SiC, MoSi_2 , MgAl_2O_4 , Mg_2Si_4 , ZrB_2 ,
15 B_2O_3 , $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$, $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, NiFe_2O_4 , Fe_3O_4 , $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, MgTiO_3 , NiTiO_3 , $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, CeO_2 , ZrO_2 , Al_2O_3 , GeO_2 , $\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$, Co_3O_4 , Nb_2O_5 , NiO/ZnO , PVP-TiO_2 , La_2CuO_4 , SiO_2 , and B_4C .

58. The composition according to claim 56, wherein said composition comprises a
20 $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ nanoparticle.

59. The composition according to claim 56, wherein said composition comprises a titania (TiO_2) nanoparticle.

25 60. A method for utilizing a nanoparticle according to any of claims 44 to 52, said method comprising applying said nanoparticle to a substrate.

61. The method according to claim 60, wherein at least one layer of said nanoparticle is applied to said substrate.

30 62. The method according to claim 60, wherein at least two layers of said nanoparticle are applied to said substrate.

63. The method according to claim 60, wherein at least three or more layers of said nanoparticle are applied to said substrate.

64. The method according to claim 60, wherein said substrate is a circuit, a capacitor,
5 or a crystal silicon wafer.

65. A method of preparing a nanoparticle, said method comprising:

a) providing a polycrystalline, ceramic nanofiber;

b) contacting said nanofiber with a solvent; and

10 c) applying energy to said nanofiber, whereby one or more nanoparticles are produced from said nanofiber.

66. The method according to claim 65, wherein said nanofiber is obtained by electrospinning a ceramic-polymer composite nanofiber from a solution.

15 67. The method according to claim 66, wherein said nanofiber is dried following said electrospinning.

20 68. The method according to claim 65, wherein said nanofiber comprises one or more of alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), barium titanate (BaTiO_3), cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), celsian ($\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$), barium osumilite ($\text{BaMg}_2\text{Al}_6\text{Si}_9\text{O}_{30}$), SiC, MoSi₂, MgAl_2O_4 , Mg_2Si_4 , ZrB_2 , B_2O_3 , $\text{Pb}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$, $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, NiFe_2O_4 , Fe_3O_4 , $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, MgTiO_3 , NiTiO_3 , $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$, CeO_2 , ZrO_2 , Al_2O_3 , GeO_2 , $\text{Mn}_2\text{O}_3\text{-Mn}_3\text{O}_4$, Co_3O_4 , Nb_2O_5 , NiO/ZnO , PVP-TiO_2 , La_2CuO_4 , SiO_2 , or B_4C .

25 69. The method according to claim 65, wherein said nanofiber has a diameter of about 10 nm to about 600 nm.

30 70. The method according to claim 65, wherein said nanofiber has a diameter of about 20 nm to about 360 nm.

71. The method according to claim 65, wherein said nanofiber has a diameter of about 10 nm to about 190 nm.

72. The method according to claim 65, wherein said nanofiber has a diameter of about 10 nm to about 170 nm.

73. The method according to claim 65, wherein said nanofiber has a diameter of about 10 nm to about 150 nm.

74. The method according to claim 65, wherein said nanofiber has a diameter of about 10 nm to about 140 nm.

75. The method according to claim 65, wherein said nanofiber has a length of about 10 nm to more than 10 m.

76. The method according to claim 65, wherein said nanofiber has a length of about 10 nm to about 1 m.

77. The method according to claim 65, wherein said nanofiber has a length of about 10 nm to about 1 mm.

78. The method according to claim 65, wherein said nanofiber has a length of about 1 mm to about 1 cm.

79. The method according to claim 65, wherein said nanofiber has a length of about 1 cm to about 1 m.

80. The method according to claim 65, wherein said nanofiber is composed of a plurality of grains or segments, wherein said grains or segments are about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm in diameter.

81. The method according to claim 65, wherein said energy in step (c) is provided by mechanical or sonic means.

5 82. The method according to claim 81, wherein said mechanical means is provided by ball milling, standard milling, attrition milling, knife milling, or rotor milling.

10 83. The method according to claim 82, wherein said milling comprises at least one grinding element.

84. The method according to claim 81, wherein said sonic means comprises high frequency sound waves.

15 85. The method according to claim 84, wherein said sound waves have a frequency of about 20,000Hz to about 23,000 Hz.

86. The method according to claim 65, wherein said nanoparticle is collected.

20 87. The method according to claim 86, wherein said nanoparticle is collected by filtering, sieving, or volatilization.

88. The method according to claim 65, wherein said nanoparticle has a diameter of about 10 nm to about 500 nm.

25 89. The method according to claim 65, wherein said nanoparticle has a diameter of about 10 nm, about 11 nm, about 12 nm, about 13 nm, about 14 nm, about 15 nm, about 16 nm, about 17 nm, about 18 nm, about 19 nm, about 20 nm, about 21 nm, about 22 nm, about 23 nm, about 24 nm, about 25 nm, about 26 nm, about 27 nm, about 28 nm, about 29 nm, about 30 nm, about 31 nm, about 32 nm, about 33 nm, about 34 nm, about 35 nm, about 36
30 nm, about 37 nm, about 38 nm, about 39 nm, about 40 nm, about 41 nm, about 42 nm, about 43 nm, about 44 nm, about 45 nm, about 46 nm, about 47 nm, about 48 nm, about 49 nm, or about 50 nm.

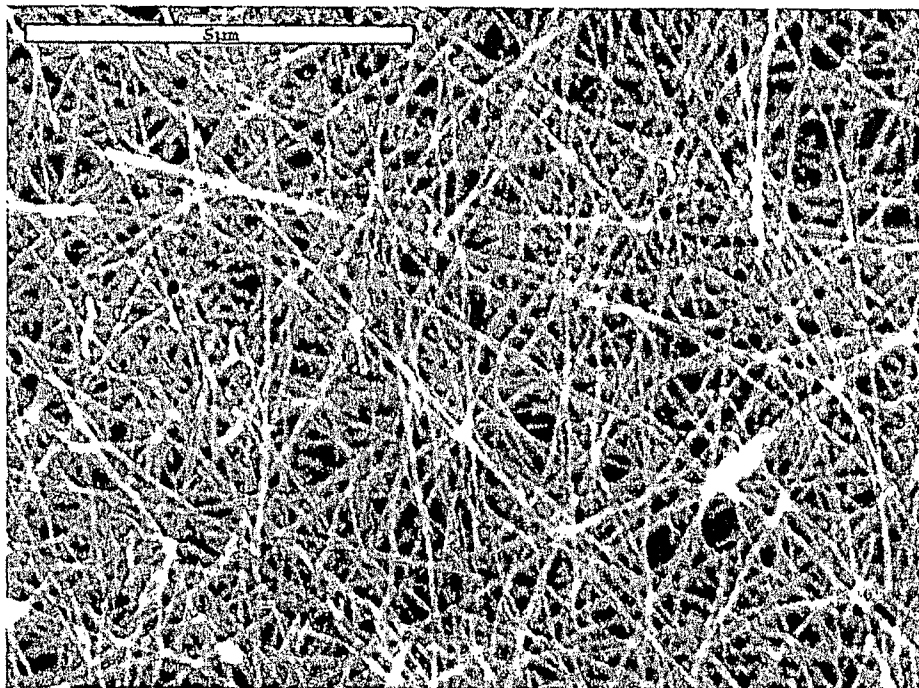


FIG. 1

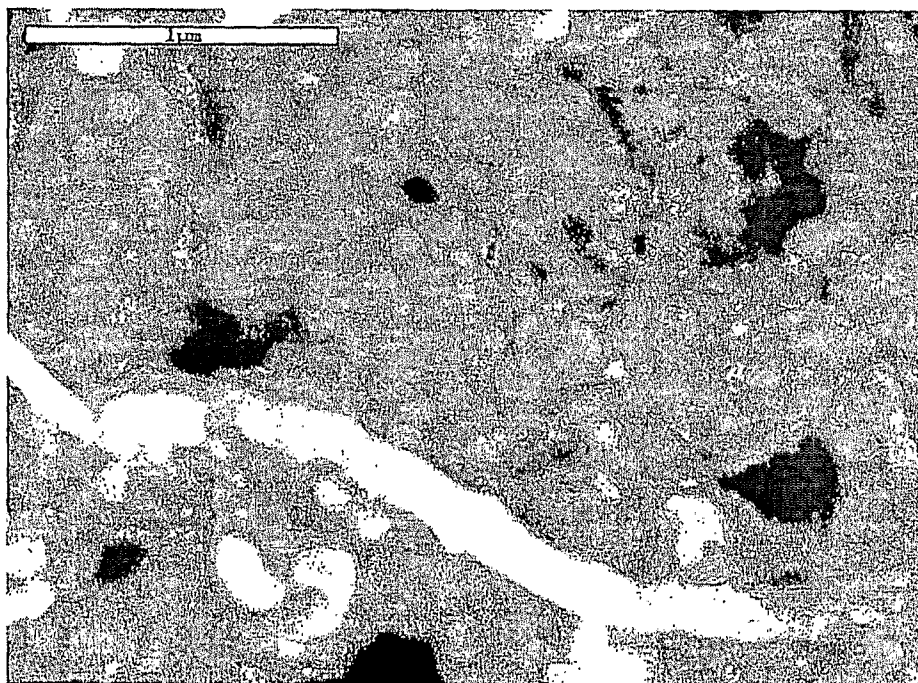


FIG. 2

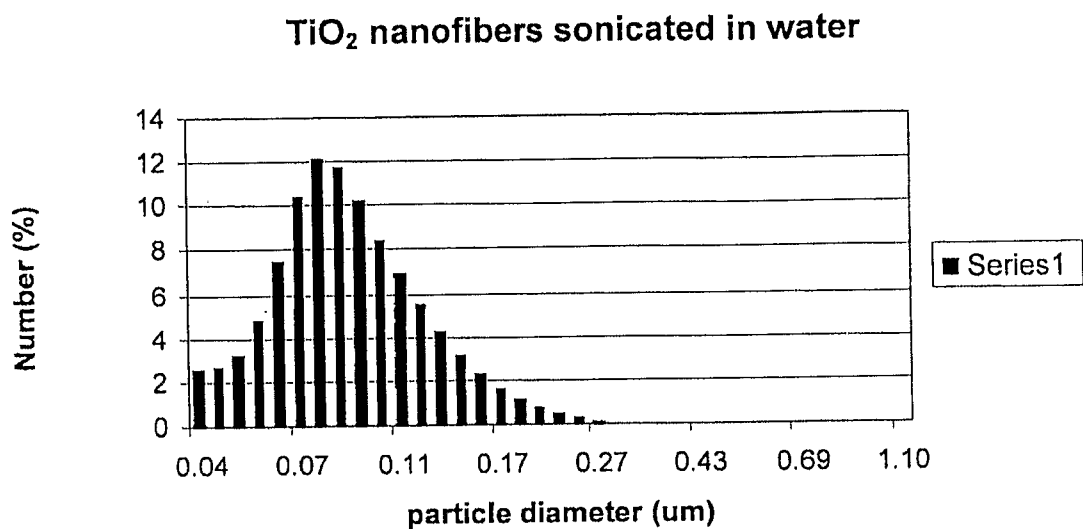
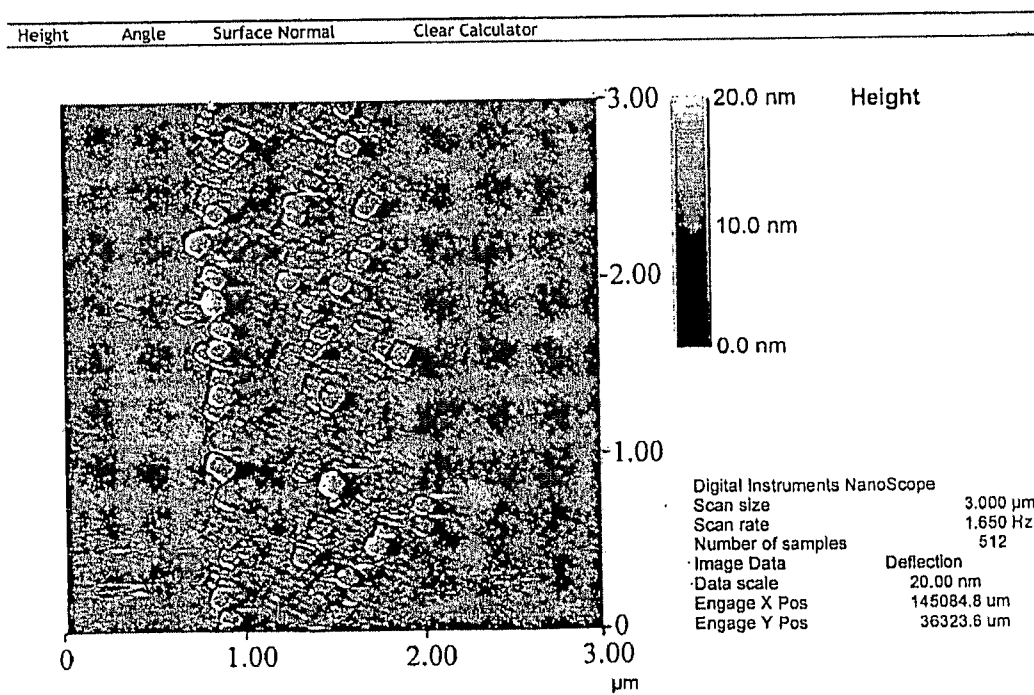


FIG. 3



bation3fl.002

FIG. 4

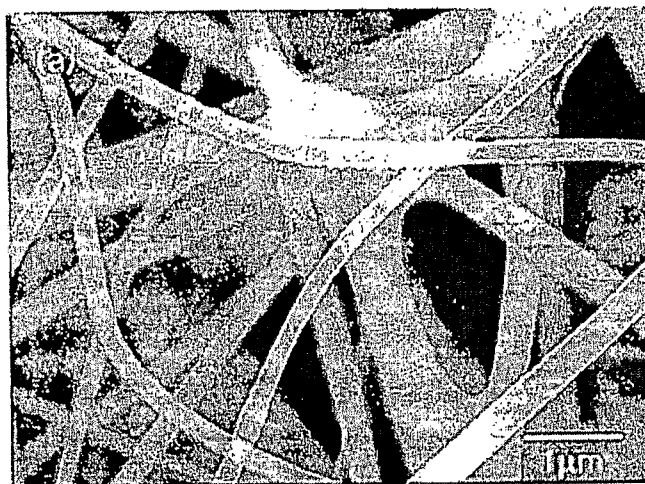


FIG. 5A

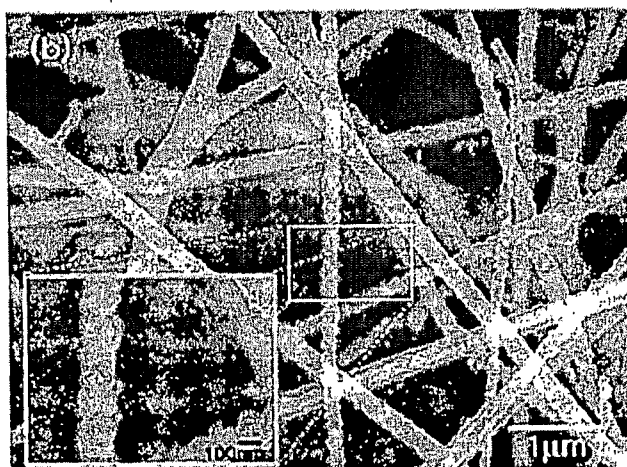


FIG. 5B

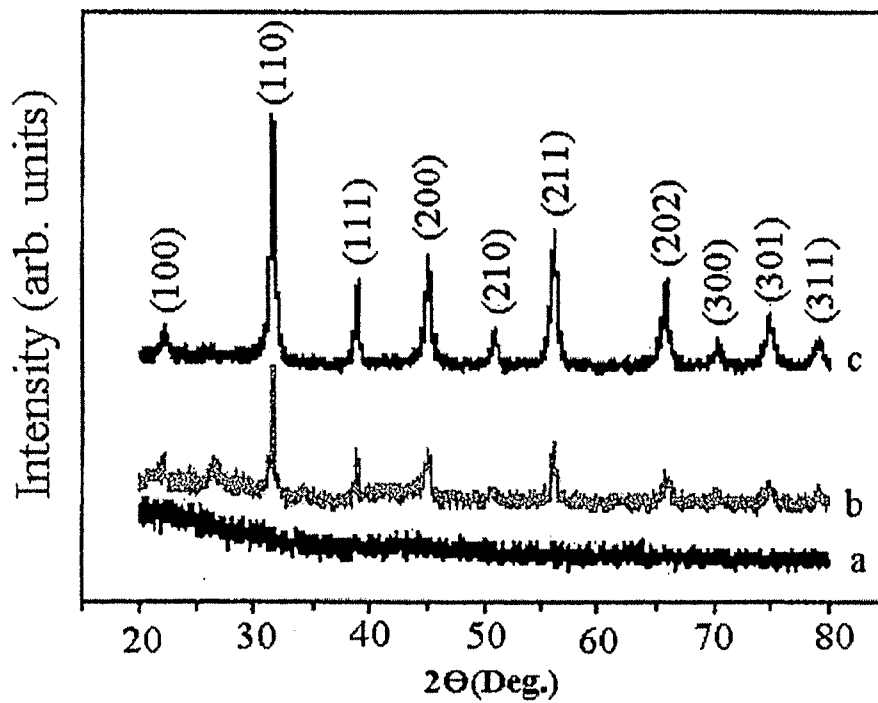


FIG. 6A-6C

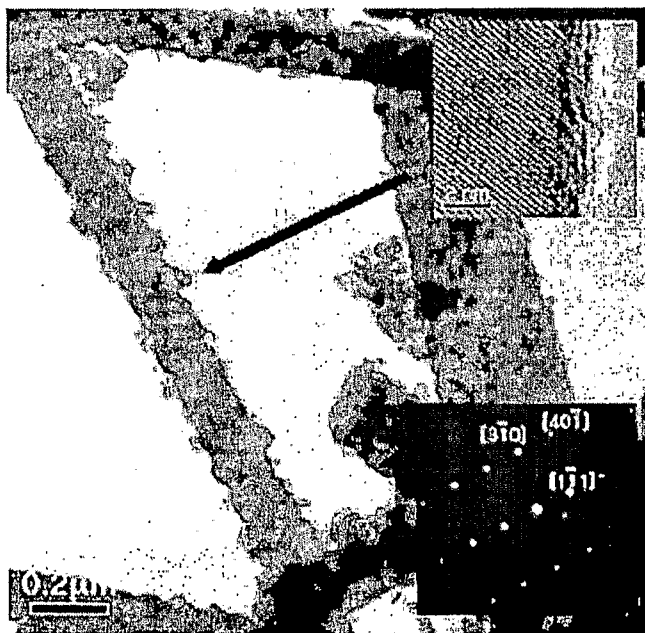


FIG. 7

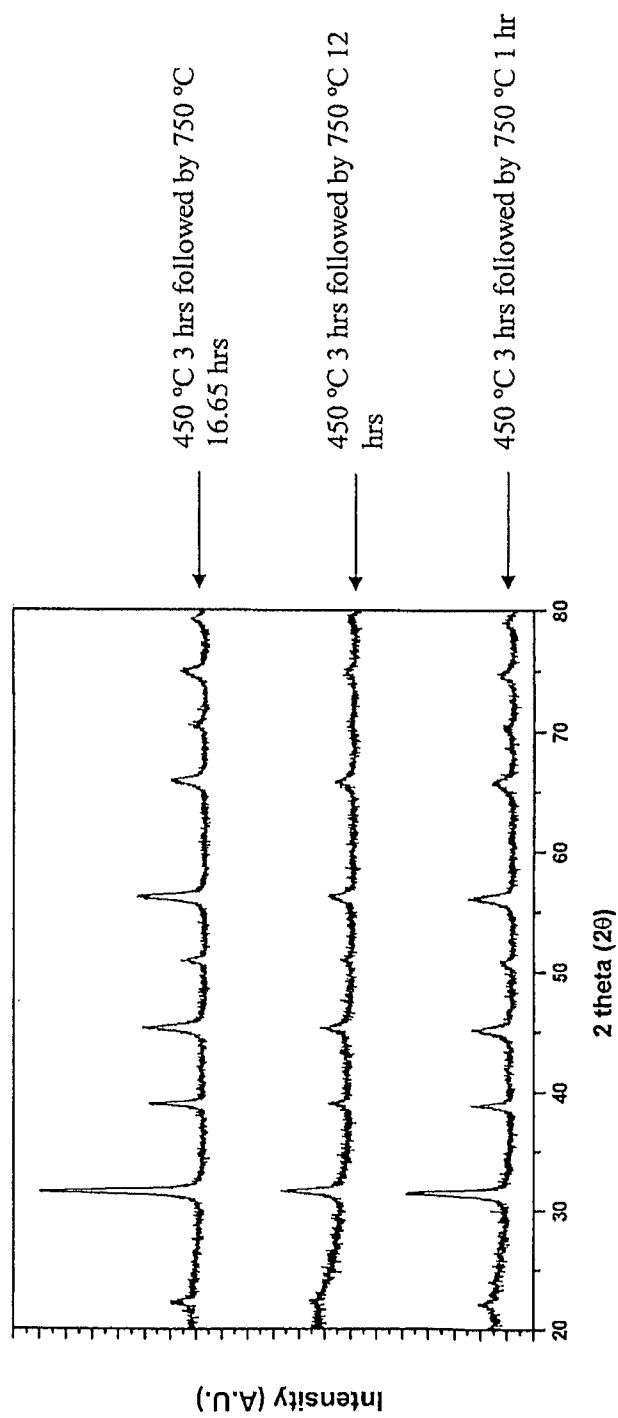


FIG. 8

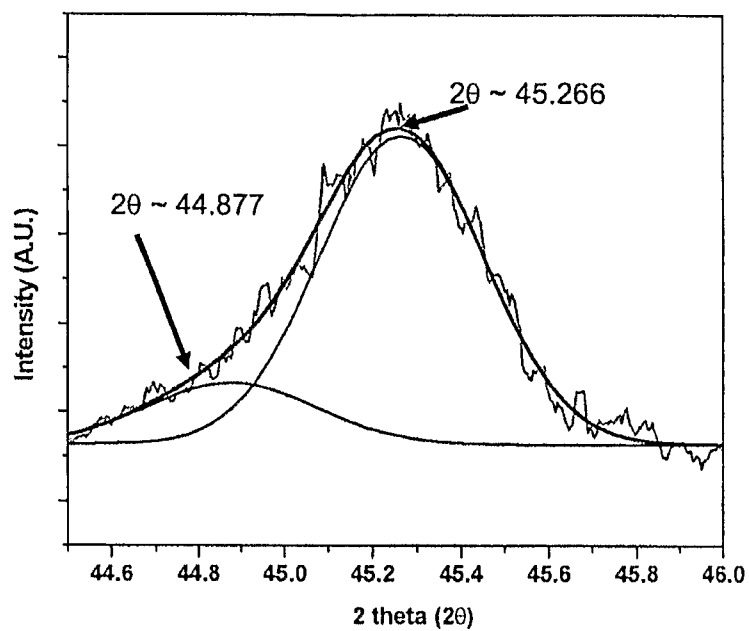


FIG. 9

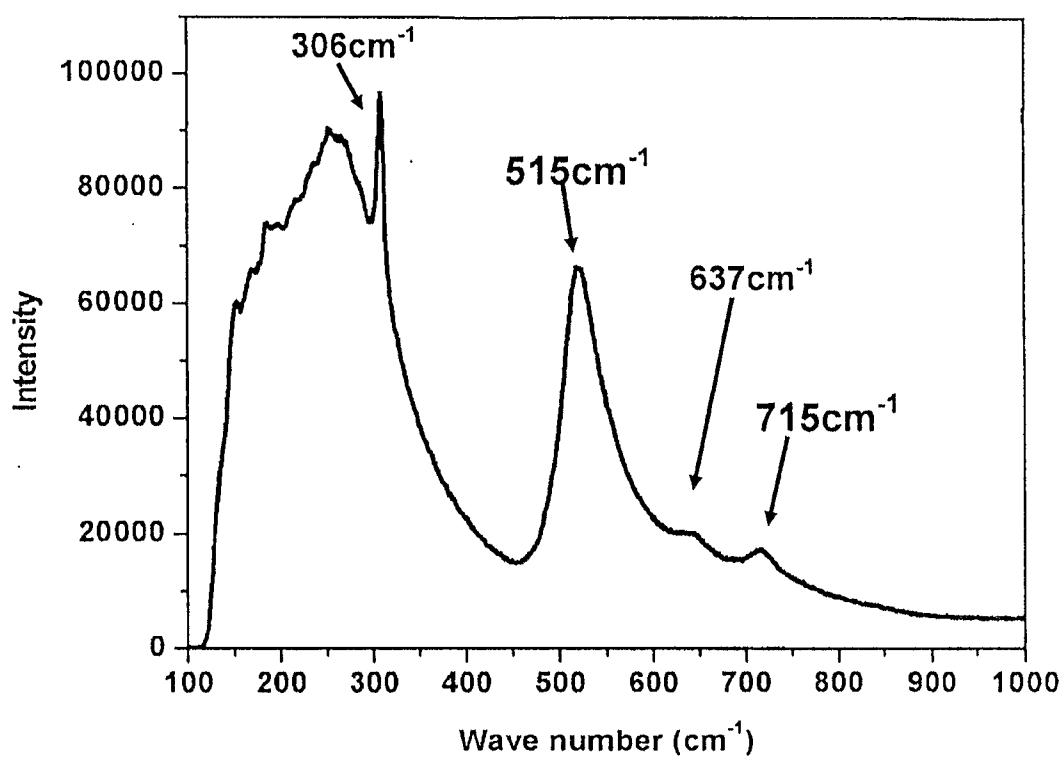


FIG. 10