

**United States Patent**            **8,298,667**  
**Smith , et al.**                    **October 30, 2012**

### **Composition and method for making a proppant**

#### **Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractures. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractures are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)  
Assignee: **Oxane Materials, Inc.** (Houston, TX)  
Appl. No.: **12/630,218** Filed: **January 27, 2009**

**United States Patent**            **D668,213**  
**Barron**                                **October 2, 2012**

### **Horizontal solar energy collector**

#### **Claims**

CLAIM I claim the ornamental design for a horizontal solar energy collector, as shown and described.

Inventors: **Barron; Andrew Ross** (Houston, TX) Assignee: **Natcore Technology, Inc.** (Red Bank, NJ)  
Appl. No.: **D/368,952** Filed: **August 31, 2010**

**United States Patent**            **D668,212**  
**Barron**                                **October 2, 2012**

### **Vertical solar energy collector**

#### **Claims**

CLAIM I claim the ornamental design for a vertical solar energy collector, as shown and described.

Inventors: **Barron; Andrew Ross** (Houston, TX) Assignee: **Natcore Technology, Inc.** (Red Bank, NJ)  
Appl. No.: **D/368,949** Filed: **August 31, 2010**

**United States Patent**            **8,217,137**  
**Barron, et al.**                    **July 10, 2012**

### **Fullerene-based amino acids**

#### **Abstract**

The present invention is directed to a series of new compounds, combining the unique properties of fullerenes and bio-active amino acid residues, and to methods for making such compounds. The present invention is directed toward fullerene-based amino acids, and to amino acid residues, peptide chains, proteins, and

polypeptides made from such fullerene-based amino acids. The present invention is further directed to amino acid residues, peptide chains, proteins, and polypeptides comprising such fullerene-based amino acids and into which such fullerene-based amino acids have been incorporated. Exemplary compounds have been prepared, and these compounds have been characterized and confirmed with infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), etc. These new compounds, which are additions to the existing amino acid residue family, may potentially possess useful pharmaceutical application and may provide a new platform for further exploration in cancer therapy, and peptide and protein engineering.

Inventors: **Barron; Andrew R.** (Houston, TX), **Yang; Jianzhong** (Missouri City, TX)

Assignee: **William Marsh Rice University** (Houston, TX)

Appl. No.: **10/585,277** Filed: **January 14, 2005**

**United States Patent**                    **8,201,517**  
**Barron, et al.**                            **June 19, 2012**

### **Method for low temperature growth of inorganic materials from solution using catalyzed growth and re-growth**

#### **Abstract**

The present invention involves a method and apparatus for depositing a silicon oxide onto a substrate from solution at low temperatures in a manner that produces homogeneous growth of the silicon oxide. The method generally comprises the following steps: (a) Chemically treating a substrate to activate it for growth of the silicon oxide. (b) Immersing the treated substrate into a bath with a reactive solution. (c) Regenerating the reactive solution to allow for continued growth of the silicon oxide. In another embodiment of the present invention, the apparatus includes a first container holding a reactive solution, a substrate on which the silicon oxide is deposited, a second container holding silica, and a means for adding silica to the reactive solution.

Inventors: **Barron; Andrew R.** (Houston, TX), **Whitsitt; Elizabeth Anne** (Houston, TX)

Assignee: **William Marsh Rice University** (Houston, TX)

Appl. No.: **12/751,434** Filed: **March 31, 2010**

**United States Patent**                    **8,168,570**  
**Barron, et al.**                            **May 1, 2012**

### **Method of manufacture and the use of a functional proppant for determination of subterranean fracture geometries**

#### **Abstract**

Proppants having added functional properties are provided, as are methods that use the proppants to track and trace the characteristics of a fracture in a geologic formation. Information obtained by the methods can be used to design a fracturing job, to increase conductivity in the fracture, and to enhance oil and gas recovery from the geologic formation. The functionalized proppants can be detected by a variety of methods utilizing, for example, an airborne magnetometer survey, ground penetrating radar, a high resolution accelerometer, a geophone, nuclear magnetic resonance, ultra-sound, impedance measurements, piezoelectric activity, radioactivity, and the like. Methods of mapping a subterranean formation are also provided and use the functionalized proppants to detect characteristics of the formation.

Inventors: **Barron; Andrew R.** (Houston, TX), **Skala; Robert D.** (Katy, TX), **Coker; Christopher E.** (Houston, TX), **Chatterjee; Dilip K.** (Rochester, NY), **Xie; Yuming** (Sugar Land, TX)

Assignee: **Oxane Materials, Inc.** (Houston, TX)

Appl. No.: **12/468,088** Filed: **May 19, 2009**

**United States Patent**            **8,075,997**  
**Smith , et al.**                    **December 13 2011**

### **Composition and method for making a proppant**

#### **Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)  
Assignee: **Oxane Materials, Inc.** (Houston, TX)  
Appl. No.: **12/961,629** Filed: **December 7, 2010**

**United States Patent**            **8,062,702**  
**Barron et al.**                    **November 22, 2011**

### **Coated fullerenes, composites and dielectrics made therefrom**

#### **Abstract**

The present invention relates to coated fullerenes comprising a layer of at least one inorganic material covering at least a portion of at least one surface of a fullerene and methods for making. The present invention further relates to composites comprising the coated fullerenes of the present invention and further comprising polymers, ceramics and/or inorganic oxides. A coated fullerene interconnect device wherein at least two fullerenes are contacting each other to form a spontaneous interconnect is also disclosed as well as methods of making. In addition, dielectric films comprising the coated fullerenes of the present invention and methods of making are further disclosed.

Inventors: **Barron; Andrew R.** (Houston, TX), **Flood; Dennis J.** (Oberlin, OH), **Whitsitt; Elizabeth** (Houston, TX) Assignee: **William Marsh Rice University** (Houston, TX)  
**Natcore Technology Inc.** (Red Bank, NJ)  
Appl. No.: **10/496,066** Filed: **November 20, 2002**

**United States Patent**            **8,012,533**  
**Smith , et al.**                    **September 6, 2011**

### **Composition and method for making a proppant**

#### **Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention.

Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)

Assignee: **Oxane Materials, Inc.** (Houston, TX)

Appl. No.: **11/728,593** Filed: **March 27, 2007**

**United States Patent**                    **8,003,212**  
**Smith , et al.**                            **August 23, 2011**

### **Composition and method for making a proppant**

#### **Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)

Assignee: **Oxane Materials, Inc.** (Houston, TX)

Appl. No.: **12/252,653** Filed: **October 16, 2008**

**United States Patent**                    **7,914,892**  
**Smith , et al.**                            **March 29, 2011**

### **Composition and method for making a proppant**

#### **Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)

Assignee: **Oxane Materials, Inc.** (Houston, TX)

Appl. No.: **12/252,581** Filed: **October 16, 2008**

**United States Patent**            **7,887,918**  
**Smith , et al.**                    **February 15, 2011**

**Composition and method for making a proppant**

**Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)  
Assignee: **Oxane Materials, Inc.** (Houston, TX)  
Appl. No.: **12/252,708** Filed: **October 16, 2008**

**United States Patent**            **7,883,773**  
**Smith , et al.**                    **February 8, 2011**

**Composition and method for making a proppant**

**Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)  
Assignee: **Oxane Materials, Inc.** (Houston, TX)  
Appl. No.: **12/252,682** Filed: **October 16, 2008**

**United States Patent**            **7,867,613**  
**Smith, et al.**                    **January 11, 2011**

**Composition and method for making a proppant**

**Abstract**

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants.

Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark**

(Raleigh, NC), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra K.** (Seattle, WA)

Assignee: **Oxane Materials, Inc.** (Houston, TX)

Appl. No.: **11/769,247** Filed: **June 27, 2007**

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**United States Patent**            **7,736,430**  
**Barron, et al.**                    **June 15, 2010**

## **Compositions and methods for controlling the setting behavior of cement slurries using carbonated fly ash**

### **Abstract**

A method of treating fly ash to modify the set time and the induction profile for a slurry comprising cement and the fly ash. The method comprising mixing fly ash with an aqueous solution comprising the calcium carbonate, thereby modifying the set time and the induction profile of the slurry comprising cement and the fly ash. A method of treating fly ash to modify the induction profile of a slurry comprising cement and the fly ash. The method comprising contacting fly ash with a wet gas stream comprising water vapor and carbon dioxide in an amount sufficient to react with the fly ash so as to modify the induction profile of the slurry comprising cement and the fly ash. Cement compositions comprising water, hydraulic cement, and carbonated fly, and associated methods of use.

Inventors: **Barron; Andrew R.** (Houston, TX), **Lupu; Corina** (Pearland, TX), **Jackson; Katherine L.** (Colonie, NY), **Bard; Sean** (College Station, TX), **Funkhouser; Gary** (Duncan, OK)

Assignee: **William Marsh Rice University** (Houston, TX)

**Halliburton Energy Services, Inc.** (Duncan, OK)

Appl. No.: **11/377,800**

Filed: **March 16, 2006**

**United States Patent**            **7,718,550**  
**Barron, et al.**                    **May 18, 2010**

## **Method for low temperature growth of inorganic materials from solution using catalyzed growth and re-growth**

### **Abstract**

The present invention involves a method and apparatus for depositing a silicon oxide onto a substrate from solution at low temperatures in a manner that produces homogeneous growth of the silicon oxide. The method generally comprises the following steps: (a) Chemically treating a substrate to activate it for growth of the silicon oxide. (b) Immersing the treated substrate into a bath with a reactive solution. (c) Regenerating the reactive solution to allow for continued growth of the silicon oxide. In another embodiment of the present invention, the apparatus includes a first container holding a reactive solution, a substrate on which the silicon oxide is deposited, a second container holding silica, and a means for adding silica to the reactive solution.

Inventors: **Barron; Andrew R.** (Houston, TX), **Whitsitt; Elizabeth Anne** (Houston, TX)

Assignee: **William Marsh Rice University** (Houston, TX)

Appl. No.: **10/535,358**

Filed: **November 18, 2003**

PCT Filed: **November 18, 2003**

PCT No.: **PCT/US03/37012**

371(c)(1),(2),(4) Date: **January 11, 2006**

PCT Pub. No.: **WO2004/047162**

PCT Pub. Date: **June 03, 2004**

**United States Patent**            **7,692,218**  
**Barron , et al.**                    **April 6, 2010**

### **Method for creating a functional interface between a nanoparticle, nanotube or nanowire, and a biological molecule or system**

#### **Abstract**

A field effect transistor and a method for making the same. In one embodiment, the field effect transistor comprises a source; a drain; a gate; at least one carbon nanotube on the gate; and a dielectric layer that coats the gate and a portion of the at least one carbon nanotube, wherein the at least one carbon nanotube has an exposed portion that is not coated with the dielectric layer, and wherein the exposed portion is functionalized with at least one indicator molecule. In other embodiments, the field effect transistor is a biochem-FET.

Inventors: **Barron; Andrew R.** (Houston, TX), **Flood; Dennis J.** (Oberlin, OH), **Whitsitt; Elizabeth A.** (Houston, TX), **Anderson; Robin E.** (Houston, TX), **Scott; Graham B. I.** (Katy, TX)

Assignee: **William Marsh Rice University** (Houston, TX)

**New Cyte, Inc.** (Sudbury, MA)

Appl. No.: **10/534,431**

Filed: **November 19, 2003**

PCT Filed: **November 19, 2003**

PCT No.: **PCT/US03/37186**

371(c)(1),(2),(4) Date: **January 24, 2006**

PCT Pub. No.: **WO2005/000735**

PCT Pub. Date: **January 06, 2005**

**United States Patent**            **7,682,527**  
**Barron , et al.**                    **March 23, 2010**

### **Fabrication of light emitting film coated fullerenes and their application for in-vivo light emission**

#### **Abstract**

A nanoparticle coated with a semiconducting material and a method for making the same. In one embodiment, the method comprises making a semiconductor coated nanoparticle comprising a layer of at least one semiconducting material covering at least a portion of at least one surface of a nanoparticle, comprising: (A) dispersing the nanoparticle under suitable conditions to provide a dispersed nanoparticle; and (B) depositing at least one semiconducting material under suitable conditions onto at least one surface of the dispersed nanoparticle to produce the semiconductor coated nanoparticle. In other embodiments, the nanoparticle comprises a fullerene. Further embodiments include the semiconducting material comprising CdS or CdSe.

Inventors: **Barron; Andrew R.** (Houston, TX), **Flood; Dennis J.** (Oberlin, OH), **Loscutova; John Ryan** (Houston, TX)

Assignee: **William Marsh Rice University** (Houston, TX)

Appl. No.: **11/834,471**

Filed: **August 6, 2007**

**United States Patent**            **7,669,658**  
**Barron , et al.**                    **March 2, 2010**

### **High strength polycrystalline ceramic spheres**

#### **Abstract**

A method for making hollow spheres of alumina or aluminate comprises: coating polymeric beads with an aqueous solution of an alumoxane, drying the beads so as to form an alumoxane coating on the beads; heating the beads to a first temperature that is sufficient to convert the alumoxane coating to an amorphous alumina or aluminate coating and is not sufficient to decompose the polymeric beads; dissolving the polymeric

bead in a solvent; removing the dissolved polymer from the amorphous alumina or aluminate coating; and heating the amorphous alumina or aluminate coating to a second temperature that is sufficient to form a hollow ceramic sphere of desired porosity and strength. The hollow spheres can be used as proppants or can be incorporated in porous membranes.

Inventors: **Barron; Andrew R.** (Houston, TX), **DeFriend; Kimberly A.** (Santa Fe, NM)

Assignee: **William Marsh Rice University** (Houston, TX)

Appl. No.: **11/612,194**

Filed: **December 18, 2006**

**United States Patent**                    **7,569,199**  
**Barron , et al.**                        **August 4, 2009**

### **Method to remove sulfur or sulfur-containing species from a source**

#### **Abstract**

High surface area iron oxides that can be ferroxane-derived iron oxides are described, as well as methods of using the same to remove at least a portion of one or more sulfur-containing species from a gas stream or liquid stream.

Inventors: **Barron; Andrew R.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Loscutova; John R.** (Houston, TX)

Assignee: **Oxane Materials, Inc.** (Houston, TX)

Appl. No.: **11/801,244**

Filed: **May 9, 2007**

**United States Patent**                    **7,491,376 B2**  
**Barron , et al.**                        **February 17, 2009**

### **Chemical derivatization of silica coated fullerenes and use of derivatized silica coated fullerenes**

#### **Abstract**

This invention is directed to a new composition of matter in the form of chemically derivatized silica coated fullerenes, including silica coated C.sub.60 molecules and silica coated carbon nanotubes, processes for making the same and to uses for the derivatized silica coated fullerenes. Included among many uses in chemical, physical or biological fields of use, but not limited thereto, are high speed, low loss electrical interconnects for nanoscale electronic devices, components and circuits. In one embodiment, this invention also provides a method for preparing silica coated fullerenes having substituents attached to the surface of silica coated fullerenes by reacting silica coated fullerenes with a wide range of organic or inorganic chemical species in a gaseous or liquid state. Preferred substituents include but are not limited to organic groups and organic groups containing heteroatoms such as oxygen, nitrogen, sulfur, and halogens. The identity of the surface functional group is chosen to provide desirable properties to the silica coated fullerenes including but not limited to solubility, miscibility, stickiness, and melting point. The present invention also describes the application of surface functionalized silica coated fullerenes as components of polymer blends and composites.

Inventors: **Barron; Andrew R.** (Houston, TX), **Flood; Dennis J.** (Oberlin, OH), **Guzelian; Andrew A.** (Belmont, MA)

Assignee: **NewCyte, Inc.** (Sudbury, MA)

Appl. No.: **11/451,110**

Filed: **June 12, 2006**

**Russia Patent 2 430 039**  
**Andrew R. Barron**    **Issued November 27, 2008**



## Method For The Low Temperature Growth Of Inorganic Materials From Solution Using Catalyzed Growth And Re-Growth

**United States Patent**            **7,459,209**  
**Smith , et al.**                    **December 2, 2008**

### Composition and method for making a proppant

#### Abstract

The present invention relates to proppants which can be used to prop open subterranean formation fractions. Proppant formulations are further disclosed which use one or more proppants of the present invention. Methods to prop open subterranean formation fractions are further disclosed. In addition, other uses for the proppants of the present invention are further disclosed, as well as methods of making the proppants. Inventors: **Smith; Russell J.** (Houston, TX), **Loscutova; John R.** (Houston, TX), **Whitsitt; Elizabeth A.** (Houston, TX), **Coker; Christopher E.** (Houston, TX), **Barron; Andrew R.** (Houston, TX), **Wiesner; Mark** (Houston, TX), **Costantino; Stephen A.** (Reading, PA), **Bordia; Rajendra Kumar** (Seattle, WA)  
Assignee: **Oxane Materials, Inc.** (Houston, TX)  
Appl. No.: **11/347,664**  
Filed: **February 3, 2006**

**United States Patent**            **7,253,014**  
**Barron , et al.**                    **August 7, 2007**

### Fabrication of light emitting film coated fullerenes and their application for in-vivo light emission

#### Abstract

A nanoparticle coated with a semiconducting material and a method for making the same. In one embodiment, the method comprises making a semiconductor coated nanoparticle comprising a layer of at least one semiconducting material covering at least a portion of at least one surface of a nanoparticle, comprising: (A) dispersing the nanoparticle under suitable conditions to provide a dispersed nanoparticle; and (B) depositing at least one semiconducting material under suitable conditions onto at least one surface of the dispersed nanoparticle to produce the semiconductor coated nanoparticle. In other embodiments, the nanoparticle comprises a fullerene. Further embodiments include the semiconducting material comprising CdS or CdSe. Inventors: **Barron; Andrew R.** (Houston, TX), **Flood; Dennis J.** (Oberlin, OH), **Loscutova; John Ryan** (Houston, TX)  
Assignee: **William Marsh Rice University** (Houston, TX)  
**Newcyte, Inc.** (Oberlin, OH)  
Appl. No.: **10/534,452**  
Filed: **November 19, 2003**  
PCT Filed: November 19, 2003  
PCT No.: PCT/US03/37188  
371(c)(1),(2),(4) Date: November 01, 2005  
PCT Pub. No.: WO20/04/046023  
PCT Pub. Date: June 03, 2004

**United States Patent**            **7,220,454**  
**Barron , et al.**                    **May 22, 2007**

### Production method of high strength polycrystalline ceramic spheres

## Abstract

A method for making hollow spheres of alumina or aluminate comprises: coating polymeric beads with an aqueous solution of an alumoxane, drying the beads so as to form an alumoxane coating on the beads; heating the beads to a first temperature that is sufficient to convert the alumoxane coating to an amorphous alumina or aluminate coating and is not sufficient to decompose the polymeric beads; dissolving the polymeric bead in a solvent; removing the dissolved polymer from the amorphous alumina or aluminate coating; and heating the amorphous alumina or aluminate coating to a second temperature that is sufficient to form a hollow ceramic sphere of desired porosity and strength. The hollow spheres can be used as proppants or can be incorporated in porous membranes.

Inventors: **Barron; Andrew R. (Houston, TX), DeFriend; Kimberly A. (Santa Fe, NM)**

Assignee: **William Marsh Rice University (Houston, TX)**

Appl. No.: **10/774,319**

Filed: **February 6, 2004**

**United States Patent**            **7,115,764**  
**Barron, Shahid**                **October 3, 2006**

## **Mechanical Shear Based Synthesis of Alumoxane Nanoparticles**

### **Abstract**

A method for forming carboxylate-alumoxane nanoparticles comprises subjecting a mixture comprising boehmite and carboxylic acid to mechanical shear. The method can be carried out at a temperature above ambient and preferably a temperature greater than 80° C., and can be carried out in the absence of a liquid phase.

Inventors: **Barron; Andrew R. (Houston, TX), Shahid; Naureen (Houston, TX)**

Assignee: **Wm. Marsh Rice University (Houston, TX)**

Appl. No.: **10/636,174**

Filed: **August 7, 2003**

**United States Patent**            **6,936,306**  
**Barron , et al.**                **August 30, 2005**

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## **Chemical control over ceramic porosity using carboxylate-alumoxanes**

### **Abstract**

This invention relates generally to a method for controlling the pore size, pore size distribution and porosity of aluminum-oxide based ceramics through the choice of substituents on carboxylate-alumoxanes and aluminum-oxide nanoparticles. The method allows for the formation of intra-granular pores in the nanometer range to be created in alumina and aluminum oxide ceramic bodies. The control over pore size and pore size distribution is accomplished through the use of different chemical substituents on the carboxylate-alumoxanes and aluminum-oxide nanoparticles. The size and distribution of pores within the alumina-oxide ceramic are dependent on the identity of the carboxylate substituents. In particular the formation of intra-versus inter-granular porosity is dependent on the identity of the carboxylate substituents. The invention also provides methods for the manufacture of ceramic coatings on ceramic and carbon fibers for composite applications and ceramic membranes with nanometer sized pores. The pore size, pore size distribution and porosity, and hence the strength, permeability and surface adhesion, of the ceramic coating is controlled by the choice of substituent on the carboxylate-alumoxane. Thermolysis of self supporting spun layers of the carboxylate-alumoxanes results in disks of alumina with controlled pore size, pore size distribution and porosity. In an alternative method a porous substrate is dipped or coated with a solution of the carboxylate-alumoxane, followed by thermolysis to produce a composite membrane.

Inventors: **Barron; Andrew R. (Houston, TX), Bailey; Diane Amy (Chicago, IL), Wiesner; Mark Robert (Houston, TX), Jones; Christopher Daniel (Houston, TX), Callender; Rhonda Lynn (Houston, TX)**  
Assignee: **William Marsh Rice University (Houston, TX)**  
Appl. No.: **09/670,230**  
Filed: **September 28, 2000**

**United States Patent 6,770,773**  
**Rose , et al. August 3, 2004**

### **Organic acid-Fe-OOH (ferroxane) particles and ferroxane-derived ceramics and ceramic membranes**

#### **Abstract**

The present invention relates to ferroxanes and a method of making wherein a ferroxane may be defined by the general formula  $[\text{Fe}(\text{O})_{\text{sub.x}}(\text{OH})_{\text{sub.y}}(\text{O}_{\text{sub.2}}\text{CR})_{\text{sub.z}}]_{\text{sub.n}}$  wherein x, y and z may be any integer or fraction such that  $2x+y+z=3$  and n may be any integer. The ferroxanes may be doped with at least one other element other than iron. The present invention further relates to a ceramic made from the ferroxanes of the present invention and a method of making. The present invention still further relates to supported and unsupported membranes made from the ceramic of the present invention.

Inventors: **Rose; Jerome (Rousset, FR), Wiesner; Mark (Houston, TX), Barron; Andrew (Houston, TX)**

Assignee: **William Marsh Rice University (Houston, TX)**

Appl. No.: **10/350,759**

Filed: **January 24, 2003**

**European Patent - France, United Kingdom 1476399**  
**German National No. 603 128 27.0**

**Rose; Jerome (Rousset, FR), Wiesner; Mark (Houston, TX), Barron; Andrew (Houston, TX)**  
**March 28, 2007**

### **Organic acid-Fe-OOH (ferroxane) particles and ferroxane-derived ceramics and ceramic membranes**

**United States Patent 6,369,183**  
**Cook , et al. April 9, 2002**

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### **Methods and materials for fabrication of alumoxane polymers**

#### **Abstract**

A composition of matter comprising: a chemically functionalized carboxylate-alumoxane that is functionalized with a chemically reactive substituent, and a reactive compound wherein the chemically reactive substituent reacts with the reactive compound to link the carboxylate-alumoxane to the reactive compound and form a polymer matrix. The functional groups on the carboxylate-alumoxane can vary depending on the desired properties of the matrix; the composition of matter may comprise a cross-linked matrix in which the cross-linked components consist of functionalized alumoxanes.

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Inventors: **Cook; Ronald Lee (Lakewood, CO); Barron; Andrew Ross (Houston, TX); Gleason; Kevin Joseph (Lafayette, CO); MacQueen; David Brent (Golden, CO); Siparsky; Georgette Laila (Denver, CO); Koide; Yoshihiro (Saitama, JP); Vogelson; Cullen Taylor (Houston, TX)**

Assignee: **Wm. Marsh Rice University (Houston, TX)**

Appl. No.: **133642**

Filed: **August 13, 1998**

**United States Patent**  
**Barron , et al.**

**6,322,890**  
**November 27, 2001**

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### **Supra-molecular alkylalumoxanes**

#### Abstract

Heterogeneous solid supra-molecular alkylalumoxanes. A supra-molecular architecture of a nano-particle foundation on which an alkylalumoxane is built. Supra-molecular alkylalumoxanes comprise (a) an aluminum-oxide nanoparticle, (b) a linkage unit, and (c) an alkylalumoxane. Supra-molecular alkylalumoxanes are prepared by the reaction of a chemically modified aluminum-oxygen nanoparticle with either a pre-formed alkylalumoxane or an alkylaluminum compound, with subsequent hydrolysis or reaction with other alkylalumoxane yielding reagents. The supra-molecular alkylalumoxanes are active as catalysts for the polymerization of organic monomers and as co-catalysts with transition metal components for the polymerization of olefins.

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Inventors: **Barron; Andrew Ross** (Houston, TX); **Obrey; Stephen J.** (Houston, TX)  
Assignee: **Wm. Marsh Rice University** (Houston, TX)  
Appl. No.: **277642**  
Filed: **March 26, 1999**

**United States Patent**  
**Kareiva , et al.**

**6,207,130**  
**March 27, 2001**

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### **Metal-exchanged carboxylato-alumoxanes and process of making metal-doped alumina**

#### Abstract

A method has been developed for the solution-based metal exchange of carboxylato-alumoxanes  $[Al(O).sub.x(OH).sub.y(O.sub.2CR).sub.z].sub.n$  with a wide range of metal cations. Metal-exchanged carboxylato-alumoxanes are new, particularly those in which about 10% to about 50% or more of the Al ions are exchanged for other metal ions. Additionally, the carboxylic acid ligands can be stripped from the boehmite core of metal-exchanged carboxylato-alumoxanes at low temperature leading to the formation of metal-exchanged boehmite particles. These new material phases can be used as intermediates for preparation of mixed metal aluminum oxide materials. Thermolysis of the metal-exchanged carboxylato-alumoxanes or metal-exchanged boehmite particles results in doped aluminas (M/Al.sub.2O.sub.3), binary (MAIO.sub.x), ternary (MM'AIO.sub.x) and even more complex metal aluminum oxide compounds, where M and M' are metal ions other than those of aluminum and are preferably those of Lanthanide metals or transition metals. The method allows preparation of pure phase materials as well as the preparation of metastable metal aluminum oxide phases. The carboxylato-alumoxanes are prepared by the reaction of boehmite (or pseudoboehmite) with carboxylic acids in a suitable solvent. Up to at least half of the aluminum cations in the boehmite lattice of the carboxylato-alumoxanes can be replaced by the reaction of metal acetylacetonates with the carboxylato-alumoxane in a suitable solvent. The metal exchange reaction can also be carried out by reaction with soluble metal salts. Reactions of boehmite with the metal acetylacetonates (or soluble metal salts) do not lead to the metal exchange reaction observed for the carboxylato-alumoxanes.

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Inventors: **Kareiva; Aivaras** (Vilnius, LT); **Bai; Chuansheng** (Clifton, NJ); **Harlan; Charles Jeffrey** (New York, NY); **MacQueen; D. Brent** (Golden, CO); **Barron; Andrew R.** (Houston, TX); **Cook; Ronald L.** (Lakewood, CO)  
Assignee: **Rice University** (Houston, TX); **TDA Research, Inc.** (Wheat Ridge, CO)  
Appl. No.: **058587**  
Filed: **April 10, 1998**

**United States Patent** **RE36,793**  
**Barron , et al.** **July 25, 2000**

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### **Stabilised olefin carbon monoxide copolymer compositions**

#### Abstract

Polymer compositions which comprise (a) a major amount of a polymer of carbon monoxide and at least one olefin and (b) a minor amount of a pseudoboehmite are stabilised against degradation in melt processing. The polymer is suitably a polyketone.

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Inventors: **Barron; Andrew Ross** (Cambridge, MA); **Davidson; Neil Shearer** (Stirling, GB); **Kneale; Brian** (Woking, GB)  
Assignee: **BP Chemicals Limited** (London, GB)  
Appl. No.: **161221**  
Filed: **September 25, 1998**  
**Related U.S. Patent Documents**

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Patent No.:	Issued:	Appl. No.:	Filed:
Reissue of: <b>05527851</b>	<b>Jun 18, 1996</b>	<b>252936</b>	<b>Jun 02, 1994</b>

**Foreign Application Priority Data**

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Jun 16, 1993[GB] 93/2356

**Current U.S. Class:** 524/437  
**Intern'l Class:** C08K 003/22  
**Field of Search:** 524/437

**United States Patent** **5,527,851**  
**Barron , et al.** **June 18, 1996**

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### **Stabilised olefin carbon monoxide copolymer compositions**

#### Abstract

Polymer compositions which comprise (a) a major amount of a polymer of carbon monoxide and at least one olefin and (b) a minor amount of a pseudoboehmite are stabilised against degradation in melt processing. The polymer is suitably a polyketone.

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Inventors: **Barron; Andrew R.** (Cambridge, MA); **Davidson; Neil S.** (Scotland, GB); **Kneale; Brian** (Surrey, GB)  
Assignee: **BP Chemicals Limited** (London, GB)  
Appl. No.: **252936**  
Filed: **June 2, 1994**

**United States Patent**  
**Barron , et al.**

**6,008,525**  
**December 28, 1999**

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**Minority carrier device comprising a passivating layer including a Group 13 element and a chalcogenide component**

Abstract

A minority carrier device includes at least one junction of at least two dissimilar materials, at least one of which is a semiconductor, and a passivating layer on at least one surface of the device. The passivating layer includes a Group 13 element and a chalcogenide component. Embodiments of the minority carrier device include, for example, laser diodes, light emitting diodes, heterojunction bipolar transistors, and solar cells.

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Inventors: **Barron; Andrew R.** (Cambridge, MA); **Hepp; Aloysius F.** (Bay Village, OH); **Jenkins; Phillip P.** (Cleveland Heights, OH); **MacInnes; Andrew N.** (Quincy, MA)

Assignee: **President and Fellows of Harvard College** (Cambridge, MA); **TriQuint Semiconductor, Inc.** (Hillsboro, OR); **The United States of America as represented by the Administrator of the** (Washington, DC)

Appl. No.: **993613**

Filed: **December 18, 1997**

**United States Patent**  
**Barron , et al.**

**5,760,462**  
**June 2, 1998**

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**Metal, passivating layer, semiconductor, field-effect transistor**

Abstract

A majority carrier device includes a bulk active region and a thin-film passivating layer on the bulk active region. The thin-film passivating layer includes a Group 13 element and a chalcogenide component. In one embodiment, the majority carrier device is a metal, passivating layer, semiconductor, field-effect transistor. The transistor includes an active layer and thin-film passivating layer on the active layer. The thin-film passivating layer includes a Group 13 element and a chalcogenide component. Source and drain contacts are disposed on the active layer or the passivating layer. A gate contact is disposed on the passivating layer between the source contact and the drain contact.

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Inventors: **Barron; Andrew R.** (Cambridge, MA); **Jenkins; Phillip P.** (Cleveland Heights, OH); **MacInnes; Andrew N.** (Quincy, MA); **Hepp; Aloysius F.** (Bay Village, OH)

Assignee: **President and Fellows of Harvard College** (Cambridge, MA); **TriQuint Semiconductor, Inc.** (Beaverton, OR)

Appl. No.: **820183**

Filed: **March 19, 1997**

**United States Patent**  
**Barron , et al.**

**5,738,721**  
**April 14, 1998**

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**Liquid precursor and method for forming a cubic-phase passivating/buffer film**

Abstract

A chemical composition consists essentially ((t-amyl)GaS).sub.4. The chemical composition can be employed as a liquid precursor for metal organic chemical vapor deposition to thereby form a cubic-phase passivating/buffer film, such as gallium sulphide.

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Inventors: **Barron; Andrew R.** (Cambridge, MA); **Power; Michael B.** (Quincy, MA); **MacInnes; Andrew N.** (Quincy, MA)  
Assignee: **President and Fellows of Harvard College** (Cambridge, MA); **Triquint Semiconductor, Inc.** (Beaverton, OR)  
Appl. No.: **418005**  
Filed: **April 6, 1995**

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**United States Patent**                      **5,300,320**  
**Barron , et al.**                              **April 5, 1994**

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### **Chemical vapor deposition from single organometallic precursors**

#### **Abstract**

A method is disclosed for forming a passivating/buffer film on a substrate. The method includes heating the substrate to a temperature which is sufficient to cause a volatilized organometallic precursor to pyrolyze and thereby form a passivating/buffer film on a substrate. The organometallic precursor is volatilized at a precursor source. A carrier gas is directed from a carrier gas source across the precursor source to conduct the volatilized precursor from the precursor source to the substrate. The volatilized precursor pyrolyzes and is deposited onto the substrate, thereby forming the passivating/buffer film on the substrate. The passivating/buffer film can be a cubic-phase passivating/buffer film. An oxide layer can also be formed on the passivating/buffer film to thereby form a composite of the substrate, the passivating/buffer film and the oxide layer. Cubic-phase passivating/buffer films formed by the method of the invention can be lattice-matched with the substrate. Electronic or electro-optical circuits or circuit elements can be formed which include passivating/buffer films formed by the method of the invention.

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Inventors: **Barron; Andrew R.** (Cambridge, MA); **Power; Michael B.** (Quincy, MA); **MacInnes; Andrew N.** (Dorchester, MA); **Hepp; Aloysius F.** (Bay Village, OH); **Jenkins; Phillip P.** (Cleveland Heights, OH)  
Assignee: **President and Fellows of Harvard College** (Cambridge, MA)  
Appl. No.: **903256**  
Filed: **June 23, 1992**  
**United States Patent**                      **5,238,711**  
**Barron , et al.**                              **\* August 24, 1993**

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### **Method of coating carbon fibers with a carbide**

#### **Abstract**

A method for rapidly providing an impervious carbon substrate such as carbon fibers with a carbide coating, in atmospheric pressure, so as to provide a carbide layer bound to the carbon substrate. A carbide layer on the impervious carbon substrate is provided by coating the substrate with a concentrated solution of a carbide forming element in compound dissolved in a suitable solvent. The carbon substrate is heated to a temperature at which the carbide forming element in compound decomposes and chemically reacts with the carbon substrate to form the desired carbide layer.

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Inventors: **Barron; Andrew R.** (Cambridge, MA); **MacInnes; Andrew N.** (Sommerville, MA); **Gilbert; Thomas R.** (Norfolk, MA)  
Assignee: **The President and Fellows of Harvard College** (Cambridge, MA)  
[\*] Notice: The portion of the term of this patent subsequent to August 23, 2009 has been disclaimed.

Appl. No.: 672378  
Filed: March 20, 1991

United States Patent 5,159,983  
Barron, et al. November 3, 1992

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### Apparatus and method for capping oil or gas wells

#### Abstract

An apparatus and method for capping a burning or blown out oil or gas well are disclosed. A pipe is placed over a flange and casing on a wellhead and welded thereto using thermite welding. The thermite reaction occurs in one or more crucibles mounted to the pipe. Graphite feeders direct the molten metal produced by the reaction into apertures near the bottom of the central pipe. The feeders join the pipe at an angle such that the molten metal flows into the annular space between the interior of the pipe and the wellhead structure in a generally circular flow pattern. A malleable clamp to conform to the configuration of the pipe and flange is provided to hold the pipe in place over the flange and act as a mold for the molten metal during the welding process. After the weld has formed, a valve in the pipe is closed, which simultaneously shuts off the flow of oil and extinguishes the fire by depriving it of oil, its fuel.

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Inventors: Barron; Andrew R. (Cambridge, MA); Cronin, Jr.; Dennis F. (Fredericksburg, VA); Manson; Paul R. (Croydon, NH)  
Assignee: Arthur D. Little Enterprises, Inc. (Cambridge, MA)  
Appl. No.: 760340  
Filed: September 16, 1991

United States Patent 5,139,999  
Gordon, et al. August 18, 1992

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### Chemical vapor deposition process where an alkaline earth metal organic precursor material is volatilized in the presence of an amine or ammonia and deposited onto a substrate

#### Abstract

A method is disclosed for the volatilization and transport of an alkaline earth metal precursor. The presence of an amine or ammonia significantly increases transport of the volatilized alkaline earth metal precursor as compared to transport under the same conditions but without the amine or ammonia.

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Inventors: Gordon; Roy G. (Cambridge, MA); Barron; Andrew R. (Cambridge, MA); Buriak; Jillian M. (Barrie, CA)  
Assignee: President and Fellows of Harvard College (Cambridge, MA)  
Appl. No.: 490756  
Filed: March 8, 1990

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### Patent Applications: United States

Method For The Low Temperature Growth Of Inorganic Materials From Solution Using Catalyzed Growth And Re-Growth  
Andrew R Barron

Application Date: 1/11/2006



**Application No.: 10/535,358**

**Coated Fullerenes, Composites And Dielectrics Made Therefrom**

**Andrew R. Barron, Dennis J. Flood, Elizabeth A. Whitsitt**

**Application Date: 11/17/2004**

**Application No.: 10/496,066**

**Fullerene Based Amino Acids**

**Andrew R. Barron, Jianzhong Yang**

**Application Date: 12/2/2008**

**Application No.: 10/585,277**

**Amplification Of Carbon Nanotubes Via Seeded-Growth Methods**

**Richard E. Smalley, Robert H. Hauge, Andrew R. Barron, James M. Tour, Howard K. Schmidt, W. Edward Billups, Christopher A. Dyke, Valerie C. Moore, Elizabeth Whitsitt, Robin A. Anderson, Ramon Colorado Jr., Michael Steward, Douglas C. Ogrin**

**Application Date: 1/31/2008**

**Application No.: 10/575,352**

**Fullerene Assisted Cell Penetrating Peptides**

**Andrew R. Barron, Jianzhong Yang, Jianhua Yang, Kuan Wang, Jonathan Driver**

**Application Date: 9/29/2008**

**Application No.: 12/294,991**

**Olefin Separation Agents And Methods Of Designing, Preparing, And Utilizing Same**

**Andrew R. Barron, John Jeffrey Allen, Christopher Eric Hamilton, Robert Schucker, Michael F. Lynch**

**Application Date: 4/14/2009**

**Application No.: 61/168,951**