The Mechanochemical Formation of Functionalized Semiconductor Nanoparticles for Electronic and Superhydrophobic Surface Applications

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ABSTRACT

A rapid, direct and efficient method for the fabrication of functionalized semiconductor nanoparticles is described. The mechanochemical method involves the simultaneous top-down formation of nanoparticles using high energy ball milling (HEBM) and reaction with a liquid medium to passivate (functionalize) the surface of nanoparticles as they are formed. In one embodiment of this process, elemental silicon is ball-milled in the presence of a reactive hydrocarbon, such as an n-alkyne. As the silicon fractures during the mechanical attrition, the formation of reactive surface species leads to the reaction with the surrounding organic medium and the creation of direct Si-C bonds. As the particles further fracture into the nano-regime and become sufficiently functionalized with organic molecules, they become soluble in the parent liquor and can be easily removed in a post-milling centrifugation step. Examples of how this method are being adapted to other semiconductors such as germanium, and other reactive organic compounds such as alkenes, alcohols, aldehydes and carboxylic acids are given. Furthermore, the adaptation of this technique to yield water-soluble analogues is elucidated. The importance of these functionalized semiconductor nanoparticles is illustrated through a brief description of the opto-electronic properties, including photoluminescence. Finally, the use of "waste" material from processing for the production of superhydrophobic films and surfaces is described. The importance of processing parameters and continuous operation to scale-up are discussed.

Keywords: mechanochemistry, nanoparticle, silicon, germanium, superhydrophobic.

1 INTRODUCTION

Fluorescent nanoparticles continue to garner tremendous interest as materials for use in optoelectronic devices [1-3] and as fluorescent biomarkers [4,5]. In semiconductor nanoparticles, such as silicon, their photoluminescent emission potentially arises from both excited states due to quantum confinement and from surface states. Although many routes to the synthesis of alkyl passivated silicon nanoparticles have been developed [6-17], most require the use of highly reactive and corrosive chemicals or the modification of nanoparticles with reactive silicon surfaces. The recent introduction of a new mechanochemical method for the production of passivated semiconductor nanoparticles [18-21] has shown this technique to be rapid, efficient and flexible. In this article, we give an overview of the types of semiconductor nanoparticles that can be produced via this method, the resulting surface functionalities, and their potential applications.

2 MATERIALS AND METHODS

2.1 Nanoparticle Passivation and Production

The production of semiconductor nanoparticles functionalized with alkyl substituents via a mechanochemical method has been described previously [18]. In brief, the semiconductor to be functionalized is placed in a high-energy ball mill (HEBM) vial along with milling balls and reactive organic compound, such as an alkyne. During the comminution process, which typically occurs over a 4-12 hour period, the semiconductor decreases in size due to particle fracture caused by impacts, and is functionalized through direct covalent bond formation between the semiconductor surface and the reactive organic compound. The process yields a solution of dissolved and functionalized nanoparticles and a "sediment" phase of larger and partially functionalized semiconductor material. These two phases are separated by centrifugation. The supernatant phase contains the nanoparticles, which can be isolated by solvent evaporation. These nanoparticles can then be dissolved in a variety of solvents for further characterization.

The process is flexible enough to accommodate a variety of metals, alloys, and semiconductors (both doped and undoped). It can also be used with a variety of functionalizing solvents such as alkynes, alkenes, aldehydes, carboxylic acids and alcohols [19]. The nanoparticles produced in this work are from either undoped silicon or germanium, and are functionalized with hydrocarbons of varying polarity.

2.2 Characterization Methods

Nuclear magnetic resonance spectroscopy (NMR) was conducted using a Bruker 300 Avance instrument. The static and dynamic contact angles were measured with a Standard Goniometer (ramé-hart Model 250) with DROPimage Advanced v2.4 and a droplet volume of 7.5 µl. The excitation-emission spectra and photoluminescence data from the nanoparticles were obtained using a Varian Cary Eclipse spectrofluorimeter. Particles were dissolved in heptane. Transmission electron microscopy (TEM) was performed using a JEOL 2011 TEM with an accelerating voltage of 200 kV.

3 RESULTS AND DISCUSSION

3.1 Alkyl-Passivated Silicon Nanoparticles

The first nanoparticles to be functionalized via this mechanochemical route were silicon nanoparticles passivated with 1-octyne [18]. These nanoparticles exhibited strong blue photoluminescence as a result of quantum confinement effects and the passivating layer. Detailed NMR studies showed that the 1-octyne was bound to the surface of silicon nanoparticles via two primary covalent bonding mechanisms: a single Si-C bond involving radical surface silicon species; and a bridging bond involving two Si-C bonds across surface double-bonded silicon species. This technique was extended to the passivation of silicon nanoparticles with octanol, octaldehye, octanoic acid, and octane [19]. These analogues also exhibited photoluminescence, but with varying intensities. The chain length of the passivating molecule can also be varied. Carbon chains of six to 12 units have been attached to silicon nanoparticles via this technique. All exhibit photoluminescence with characteristic Stokes shifts (see example of hexyne-capped Si nanopoarticles in Fig. 1).

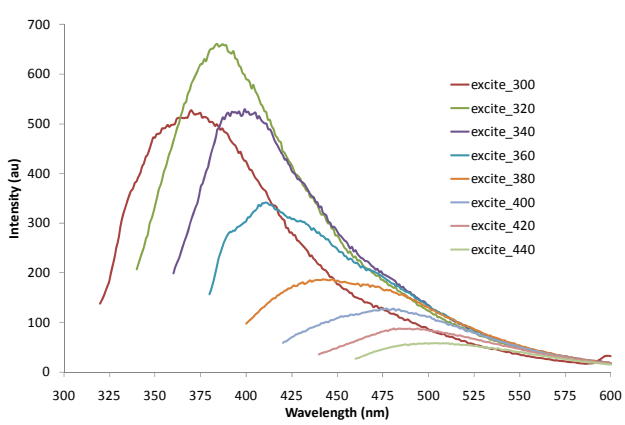

Figure 1 Photoluminescence (PL) emission spectra of fractionated hexyne-capped silicon nanoparticles at various excitation wavelengths.

The technique is now being extended to bi-functional alkyl chains. For example, milling in 1,7 octadiene results in not only a covalent bond with the silicon surface atoms, but also a terminal double bond (see Fig. 2) which can be utilized for further reactions with surface chain termini. Similar bifunctional molecules such as octadiyne, chlorooctyne, and valeric/pimelic acid can be utilized to produce nanoparticles capped with triples bonds, –Cl, and –COOH groups at the chain termini, respectively.

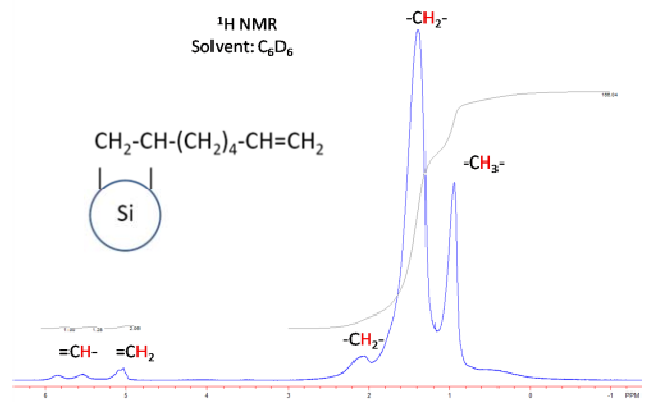

Figure 2 Proton NMR of silicon nanoparticles functionalized with 1,7 octadiene.

3.2 Alkenyl-Passivated Germanium Nanoparticles

Reactions analogous to those conducted with silicon can be carried out with germanium as the base semiconductor [21]. As with silicon, passivated nanoparticles in the ~5 nm regime are formed (see Fig. 3). There is a particle size distribution that results with this technique, but filtering and chromatographic techniques can be employed to narrow the size distribution.

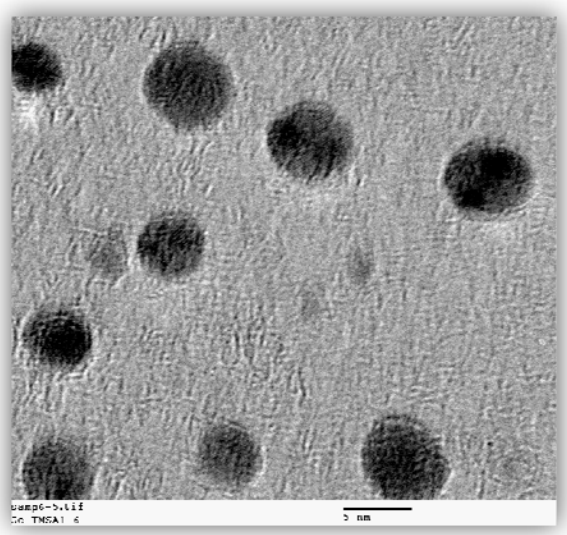

Figure 3 TEM photomicrographs of alkenyl-passivated germanium nanoparticles.

3.3 Water-Soluble Nanoparticles

Water-soluble semiconductor nanoparticles can be made by manipulating the passivating agent and its chain-end chemistry. There are several such chemical routes currently being studied. By utilizing the bi-functional passivating molecules referred to in section 3.1., water-soluble nanoparticles can be made through click chemistry approaches. In one such embodiment, chloro-terminated alkyl chains can be converted to primary amines via Gabriel [22] (see Fig. 4) or Williamson ether [23] synthesis routes.

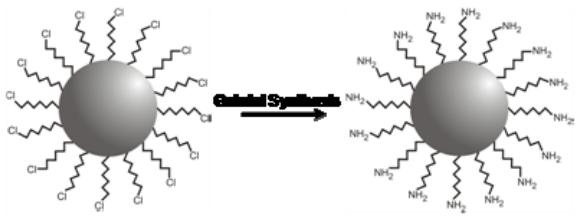

Figure 4 Synthetic route to formation of amine-capped silicon nanoparticles.

3.4 Superhydrophobic Films

Material that is not sufficiently functionalized or is too large to be solubilized in the surround reactive liquid can be separated via centrifugation and is referred to as "sediment." The sediment phase still contains a large quantity of passivated silicon, albeit larger in diameter with less surface coverage than the nanoparticles in solution. These functionalized particles are nevertheless useful for the production of superhydrophobic surface. Films of alkyl-passivated silicon nanoparticles are easily produced from the sediment phase by spreading a concentrated suspension on glass slides and evaporating the solvent. The resulting films have been shown to have high water contact angles (> 150°, see Fig. 5) [20]. Their contact angle hysteresis is still too high for superhydrophobic applications, and their mechanical integrity must be improved, but initial results are encouraging that the sediment phase can also lead to useful products.

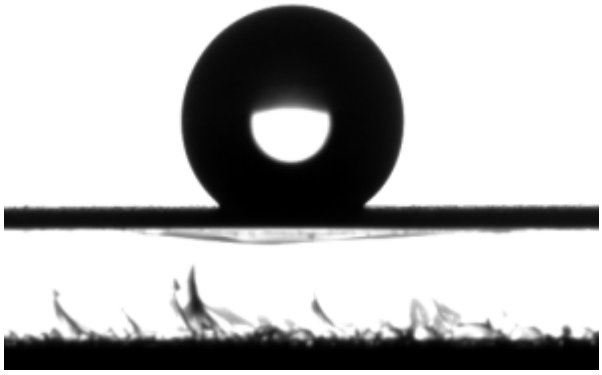

Figure 5 Static contact angle of water on passivated silicon particle film.

4 CONCLUSIONS

A rapid, direct and efficient method for the fabrication of functionalized semiconductor nanoparticles is described. The method has been demonstrated for both silicon and germanium nanoparticles, with surface passivating species comprising alkynes, alkenes, alcohols, aldehydes, carboxylic acids of varying chain length (6-12 carbon units), and their bi- and multi-functional analogues. All nanoparticles produced via this technique exhibit some photoluminescence, and can be fractionated using filtration and chromatographic separation techniques.

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