Facile graphitization of silicon nano-particles with ethanol based chemical vapor deposition

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HIGHLIGHTS

- Formation of graphitic carbon over Si NPs using ethanol as a feedstock in CVD.
- Graphene layer number can be tailored.
- Growth through oxide surface layer of Si NPs (catalytic effect).
- Graphitization process using ethanol can occur at lower temperatures than methane.

GRAPHICAL ABSTRACT
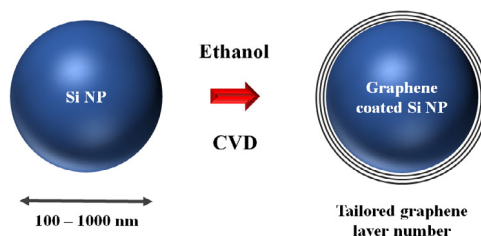
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ABSTRACT

There is a growing demand for nanoparticles coated with graphene due their promise in various applications such as batteries and supercapacitors, sorbents, and biomedical applications. A good example is Si where its combination with carbon is considered important for electronics and energy applications, such as lithium ion batteries, polymer based composites and even bio-medical applications. In this study, we aim to develop a very simple chemical vapor deposition approach to form graphitized Si nanoparticles in which ethanol serves as the C feedstock. This differs from other CVD approaches which tend to use a gaseous hydrocarbon (e.g. CH_4) as the carbon feedstock. The use of ethanol in which Ar is simply bubbled through liquid ethanol leads to a simpler and cheaper approach. Moreover, in conventional CVD, often an oxidant (e.g. CO_2) is added to aid graphitization and minimize the formation of SiC at the Si surface. Ethanol provides a source of O which serves as an inbuilt oxidizer to aid graphitization and limit the formation of SiC. The simple synthesis approach allows one to tailor the number of graphene layers coating the Si nanoparticles through the three main synthesis parameters of ethanol supply, temperature and reaction time. Moreover, using ethanol as the precursor, lower graphitization temperatures than for methane can be used.

1. Introduction

Among the many nano-materials developed, nanoparticles (NPs) are perhaps one of the most successful in commercial applications. A growing sector of nanoparticles is carbon encapsulated nanoparticles. Typical carbon encapsulated NPs are encapsulated with a number graphene layers. Graphene encapsulated NPs can be used in sorbents [1], supercapacitors [2], batteries [3–8], hydrogen

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storage [9], pollutant removal [10], water remediation [11] and various biomedical applications such as hyperthermia [12], bio-imaging [13], drug delivery [14–16] and biosensors [17,18].

Graphene encapsulated NPs can be prepared through a number of synthesis routes. A more common route is by chemical vapor deposition (CVD) [19–27]. Another widespread approach is through electrostatic assembly [28,29]. Other examples include the aerosol method [30] and the hydrothermal method [31,32].

In the CVD method, a precursor gas flowing into a heated surface in an enclosed chamber is coated by the deposition stock, in this case carbon. The technique is well established and is attractive in that it is relatively easy to scale up. For the graphitization process a wide variety of C precursors are available and can be solid, liquid or gaseous. In this work, we look at the use of ethanol as the feedstock. The use of ethanol has been exploited often in the synthesis of carbon nanotubes [33]. It can also be used for the synthesis of graphene in both thermal CVD and Plasma CVD [34]. CVD is attractive as a synthesis approach because it is well established within industry and is suitable for large scale production. Moreover, it is also easily available in laboratories as a research tool and so has gained enormously in popularity both commercially and academically [35]. In our CVD approach using ethanol as the feedstock, it allows a very easy experimental set up and so is both facile and cost effective. Toxins are negligible and it can easily be scaled up. In our CVD, ethanol is fed into the reaction chamber by bubbling Ar through the liquid ethanol, thus yielding Ar somewhat saturated with ethanol vapor. We look to graphitize Si NPs. The combination of Si and C is important for their potential in electronic devices [36,37] and in Li ion batteries [38–41] and supercapacitors [42–46]. Hence it is important to find production methods that are simple and are suitable for large scale fabrication. To this end we explore the use of a simple ethanol based CVD approach for the graphitization of Si NPs. Ethanol is chosen not only because it is an easily available solvent, but also because it contains oxygen. Oxygen has been shown to help the graphitization in various works [47–49]. Moreover, we show that ethanol can graphitize at lower temperatures than the more commonly used methane feedstock. In addition, having an oxidant present in the reaction can help reduce or even prevent the formation of SiC at the Si NP surface. Our studies suggest little to no SiC formation in our synthesis approach.

2. Methods

2.1. Chemical vapor deposition

The Si NPs for the CVD reaction were purchased from Aladdin Industrial Corporation (purity of 99.9% (metal basis)). The claimed NP size was 100–120 nm which as somewhat smaller than our measured values for the NPs (see main text). For the chemical vapor deposition (CVD) reaction, a horizontal tube furnace (MTI 1100) was used. High purity ethanol was used as the carbon feedstock in its as received form, which was placed in a bubble unit. Ar could introduced into the system via two routes. One route was used to transport the ethanol vapor into the reactor via bubbling unit. This route run at 50 sccm and 100 sccm. While the other route was used to maintain inert atmosphere in the reactor at constant flow of Ar at ca. 200 sccm. Thus, the total flow rates of Ar flowed into the system were 250 sccm and 300 sccm. The ethanol content was flowed into the quartz tube at ca. 0.02 sccm (ca. 3 wt%) and ca. 0.04 sccm (ca. 5 wt%) for 50 and 100 sccm respectively. The reaction pressure was maintained at ca. 1 bar pressure. Prior to the reaction, the quartz reactor tube and the substrate, the ceramic boat used for holding the Si NPs, were heated up in air to 1000 °C to burn off contaminants in the system. For the CVD reaction, the clean boat was filled with 20 mg of Si NPs and then placed at the center of
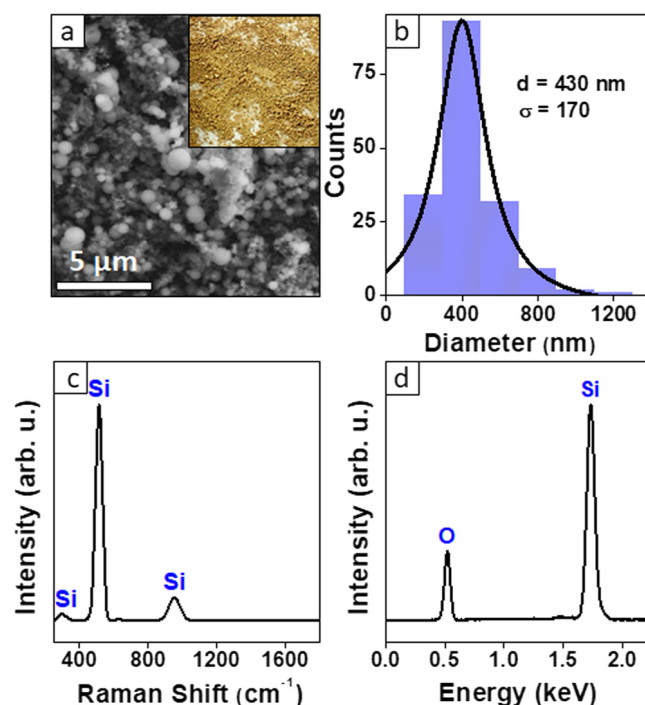
Fig. 1. Characterization of silicon nanoparticles (Si NPs) used in the CVD reaction: (a) SEM image, Scale: 5 μm. Inset: image of original sample; (b) Sample size distribution using SEM data; (c) Raman spectra showing both first and second order excitation of silicon NPs; (d) EDS data showing presence of silicon with a little amount of oxygen.

the reactor. Initially, the system was flushed with pure Ar. After that, ethanol was also introduced into the reactor via bubbling unit. The system then heated up to the desired temperature and then maintained at this temperature for 30, 60 or 90 min. The explored reaction temperatures were 850 °C, 900 °C, 950 °C and 1000 °C. After reaction, the system was cooled down naturally in a flow of pure Ar. Once cooled to room temperature the samples were removed and prepared for multiple characterizations in their as-produced form with no washing.

2.2. Characterization

The Raman characterizations were completed using Horiba (Confocal LabRAM HR 800). The laser wavelength was 514 nm with a power of ca. 4 mW. The Fourier Transform Infrared (FTIR) data was collected on a Tensor 27 spectrometer from Bruker Optics. Scanning electron microscopy (SEM) micrographs and energy dispersive spectroscopy (EDS) were obtained on a Hitachi SU 8010. Transmission electron microscopy (TEM), including EDS, was collected on an FEI Tecani F30 operating with an acceleration voltage of 80 kV. Thermo-gravimetric analysis (TGA) as carried out on a SII Nanotechnology Co. Ltd, TG/DTA 7300 unit (using synthetic air).

The thermodynamic calculations were achieved using software developed by the National Aeronautics and Space Agency (NASA). The program, CEA (Chemical Equilibrium with Applications) can calculate the chemical equilibrium compositions and properties of complex mixtures [50]. The parameters used in this work included 3 wt% ethanol vapors used as carbon precursor under pure Ar or forming gas (3 vol% of H_2 gas in Ar) at constant reaction temperature and pressure conditions.

3. Results and discussion

Fig. 1 shows the characterizations of the as-purchased Si NPs. Panel a shows an SEM micrograph of the starting material with an