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Highly ordered carbon-based nanospheres with high stiffness

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ABSTRACT

Understanding properties of individual nanostructures, such as mechanical properties and deformation mechanism, aid to control their properties for specific applications. Here we report, the mechanical properties of individual boron and nitrogen doped carbon-based nanospheres (CNS) using in-situ nano-compression testing in a scanning electron microscopy (SEM). The in-situ SEM characterizations showed classical sphere deformation during initial loading and it can be deformed till 40–50 percent. Elastic modulus of spheres is 33.3 GPa which has been determined using unloading curves. The mechanical properties of CNS structures are quite outstanding when it is compared to some other conventional nanomaterials such as polymer-based spheres and nanotube structures.

1. Introduction

During last two decades the discovery of carbon nanomaterials such as fullerene, carbon nanotube and graphene opened a new era due to their exciting properties [1–3]. Carbon-based nanomaterials with highly curved graphitic structures, high electrical conductivity, thermal stability, high oxidation resistance, and superior mechanical properties are desirable for a broad range of applications such as environmental, biomedical and energy applications [4–7]. Among nanostructured carbon-based materials carbon nanospheres (CNS) have attracted great attentions since they have outstanding chemical stability, low density, as well as high compressive strength [8–12]. CNS structures have a broad range of applications such as supercapacitors, Li-ion batteries, biosensors, catalyst and drug-delivery [13–15].

Production of CNS structures broadly can be categorized into two types, high temperature synthesis such as chemical vapor deposition (CVD), arc-discharge and the low temperature pyrolysis and catalytic decomposition of organic compounds. For example, Chen and co-worker reported production of CNS using microwave assisted reaction followed by thermal treatment in ammonia atmosphere [16]. Another work about carbon-based spheres reported by W. Xiong et al. They reported synthesis of carbon-based spheres using hydrothermal method and demonstrated as supercapacitor electrodes [15]. In all types of productions, it is one of the most important requirements to control their properties for specific applications. Toward this aim, the properties of single nanomaterials must be understood well. Understanding the deformation mechanism of individual CNS will help us in engineering the 3D structure. Nanoindentation is the only viable and effective approach to measure their mechanical properties of small-sized nanomaterials [17–21]. Till now variety of work about in-situ mechanical properties of nano/micro spheres have been reported [22–24]. In most of these reports, AFM has been used to measure mechanical properties of the nanostructures. However the AFM tip and its geometry are critical in such test and need further processing using several models to incorporate its affect, which leads to an indirect measurement of the modulus value [13,14]. For example, Armini and co-worker employed AFM tip to measure mechanical properties of polymethylmethacrylate (PMMA) polymers and polymer coated silica-shell particles [25]. Another work involving compression of polymer-based microspheres using AFM

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tip has been reported by Tan and co-workers [26]. They calculated the surface modulus of polystyrene particles from the deformation of microspheres using AFM tip [26]. In addition of AFM, in-situ SEM and TEM can be used to measure mechanical properties of individual nanomaterials [27–29]. For example, Shan et al. used in-situ compression test in a TEM to determine mechanical properties of CdS nanoparticles [28]. They showed that high stress and strain of the CdS spheres are the result of their hierarchical structures. In the other report, Hao et al. used in-situ a hybrid scanning electron microscopy/scanning probe microscope (SEM/SPM) system to obtain the force–displacement curves and they calculated Young's modulus of microspheres based on Hertz's contact theory mechanics. Their results showed that Young's modulus of a polycrystalline TiO_2 microspheres were approximately 30% larger than the bulk materials [22]. Even there are a few reported studies, it still remains a big challenge to conduct mechanical properties of individual nanospheres. Here we report the mechanical testing of boron (B) and nitrogen (N) doped carbon-based single sphere using flat punch in-situ indenter attached with SEM.

2. Experimental section

CNS structures in this report is produced using chemical vapor deposition (CVD) method. In typical CVD process, they are fabricated with introducing mixture of ammonia borane, ferrocene in dichlorobenzene under Ar/H_2 as a carrier gases at 1000 °C (Fig. 1a–c). As a result of the CVD reaction, boron (B) and nitrogen (N) doped CNS structures produced and collected from the surface of the quartz tube. The obtained material was characterized using scanning electron microscopy (SEM), contact angle measurement, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), fourier-transformed infrared spectroscopy, thermogravimetric analysis (TGA), BET surface analyzer and transmission electron microscopy (TEM) and in-situ compression test in scanning electron microscopy (SEM). Additionally, we demonstrate CNS structures as an anode material for Li-ion battery application.

3. Results and discussion

In ordered to understand the morphology of the obtained material is characterized with SEM. As shown in Fig. 1d shows the entirely packed macroscopic structure of the acquired CNS. Fig. 1e shows that the nano-sized interconnected CNS structures, thus these interconnection results highly porous framework which is superhydrophobic (122°) and light weight. Additionally, the macrostructure of CNS are perfectly shaped and consist of not only individual, also interconnected structures (Fig. 1f). The diameters of spheres are ranging between 50 nm and 250 nm.

The Raman spectra of CNS can be seen in Fig. 2a that shows two main peaks: the first peak is represents the graphitic layer (G-band) at 1592 cm^{-1}, which is related to sp^2 vibrations of CNS. The second peak at 1351 cm^{-1} (D-band) indicative of sp^3 hybridization of CNS (Fig. 1a) [30,31]. The defect density on the surface of the structure can be determined from the ratio between I_D:I_G bands. The relative

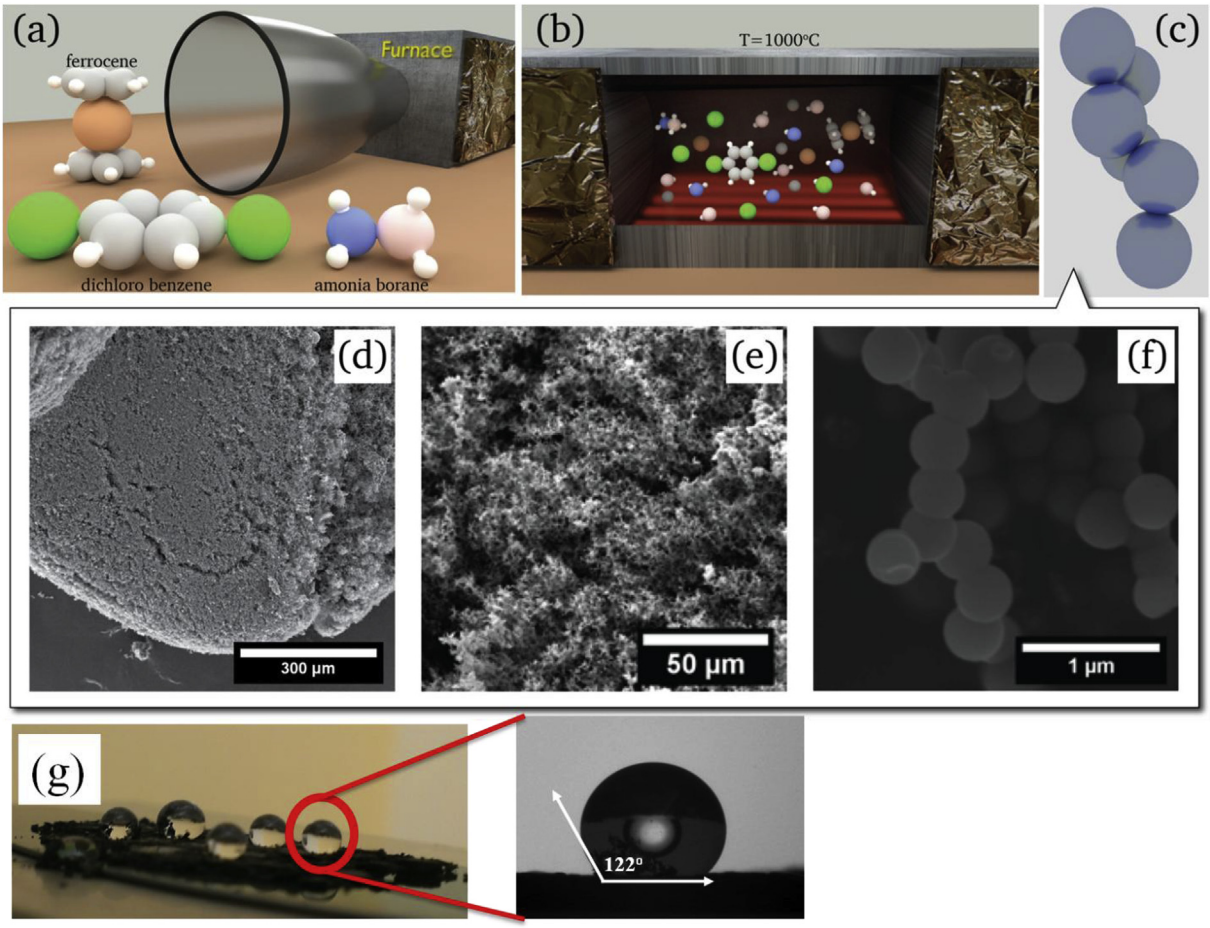

Fig. 1. (a, b) Synthesis procedure of CNS, ammonia borane, ferrocene in dichlorobenzene under Ar/H_2 as a carrier gases purged to CVD at 1000 °C, (c) results CNS, spheres. (d, e, f) scanning electron microscopy images of spherical structures. (g) wettability properties of the as grown spheres. (A colour version of this figure can be viewed online.)