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.

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 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 microscope/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 TiO₂ 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.

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 amonia borane, ferrocene

in dichlorobenzene under Ar/H₂ as a carrier gases at 1000 °C (Figure 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 microscope (SEM). Additionally, we demonstrate CNS structures as an anode material for Li-ion battery application.

RESULTS AND DISCUSSION

In ordered to understand the morphology of the obtained material is characterized with SEM. As shown in figure 1d shows the entirely packed macroscopic structure of the acquired CNS. Figure 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 (Figure 1f). The diameters of spheres are ranging between 50nm to 250nm.

The Raman spectra of CNS can be seen in figure 2a that shows two main peaks: the first peak is represents the graphitic layer (G-band) at 1592 cm⁻¹, which is related to sp² vibrations of CNS. The second peak at 1351 cm⁻¹(D-band) indicative of sp³ hybridization of CNS (Figure 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 intensity ratio of these two band (I_D:I_G :0.85) is regarded the degree of graphitization. XPS analysis was used for quantitative chemical analysis of CNS (Figure 2b). The C1s core level peak positions of the carbon atoms are at 283.7 eV. The peaks at binding

energy near 284.3 eV and 283.6 eV are considered to be due to B-C and C-N bonding, respectively [32]. The Fourier transform infrared spectroscopy (FT-IR) of CNS shows in figure 2c. The peak at 912 cm^{-1} is attributed to B-N-B bending mode and the peak at 1382 cm^{-1} represents B-N stretching modes of BCN [33]. The peak at around 1071 cm^{-1} is corresponding to the B-C vibrations [34]. The peak around 1600 cm^{-1} split to two parts; the peak at 1604 cm^{-1} is corresponding to sp^2 C-N bond vibration and the one at 1646 cm^{-1} is attributed to -C=C- stretching [35, 36]. Thermo-gravimetric analysis (TGA) data showing weight loss of CNS as a function of temperature between 30°C and 800°C ($10^\circ\text{C}/\text{min}$, air atmosphere). The negative of the first derivative ($^\circ\text{C}$) is also plotted as a function of temperature. As shown in figure 2d, the CNS is thermally stable until around $\sim 540^\circ\text{C}$ and 89% of the material decomposes until $\sim 660^\circ\text{C}$. The derivative weight loss as a function of the temperature shows that there are two overlapping steps to the CBN breakdown. These two steps show that the samples consist of two components which have similar decomposition temperature. Compared to some other carbon-based nanomaterials, CNS structures are thermally more stable. For example, decomposition temperature of some reported CNTs is around below 600°C [37, 38]. BET surface analysis was conducted to determine the surface area, porosity of the CNS structures (Figure 2e). Porous materials can be classified in three categories; materials with pore diameter are less than 2nm is microporous. If pore sizes are between 2 and 50 nm, it is mesoporous and pore diameter larger than 50 nm is called macroporous. CNS samples were degassed for 18 hours at 200°C , and then BET surface analysis carried out. The N_2 absorption can be classified as a type-I isotherm that exhibits the mesoporous structure of the CNS structures (Figure 2e). From the adsorption isotherm, the surface area of the CNS sample is $98.8\text{ m}^2/\text{g}$. The inserted figure in figure 2e shows that the average pore diameter of CNS structure is 3.3 nm which point to mesoporous structures.

In order to get detail information about CNS structures, detailed transmission electron microscopy (TEM) (Figure 3). As a result of TEM investigations, it clearly can be seen CNS are perfectly shaped (Figure 3a, b) and these nicely shaped spherical B and N doped carbon-based spheres are interconnected (Figure 3c). Besides TEM imaging, elemental mapping in TEM also performed to get information about distribution of doped elements. It clearly revealed the presence and uniform distribution of carbon, boron and nitrogen (Figure 3d).

Nanomechanical compression tests on individual CNS particles were conducted using an *in situ* SEM instrument, PI 85 PicoIndenter (Hysitron, USA) (Figure 4a). The particles were dispersed on Si substrate from solution, were compressed using 1 μm diamond probe in load-control mode with a loading rate of 5 $\mu\text{N/s}$ to a peak load of 100 μN . In all the tests, the load-displacement data and the real-time video of deformation were synchronized and captured simultaneously, which aided the post-experimental analysis. Figure 4b-c shows typical load-displacement data from 200 nm particles. The elastic modulus was determined from the unloading curves using [39].

$$E = (1/2r_c) \cdot dP_s/dh, \quad (1)$$

Where c is the contact radius, P_s is the applied load during unloading and d is the displacement during unloading. Using the equation, the average elastic modulus was calculated to be 33.3 ± 1.5 GPa. The sequence of images that are taken from the video is shown in figure 4c. The SEM images shows classical sphere deformation during initial loading and it can be deformed till 40-50 percent. There is plastic deformation followed by fracturing can be observed at the top half the sphere. It can be observed that surface layer on the particles is peeled off from the core layer during deformation. The fractured shape clearly shows hollow structure inside.

A comparative plot of the elastic modulus of CNS with polystyrene (PS) (2.9 ± 0.4 GPa) [8], PS/SiO₂ composite (6.0 ± 1.2 GPa) [8], PS/CeO₂ composite (7.93 GPa) [40], polymethylmethacrylate (PMMA) (4.3 ± 0.7 GPa) and PMMA/SiO₂ composite (4.5 ± 0.7) [25] shown in Figure 4d. . It clearly shows the elastic modulus of CNS is higher than above materials and very close to boron nitride nanotubes (BNNT) and carbon nanotubes (CNT) [41, 42].

The electrochemical measurements were performed by using 2032-type coin cells that were assembled in an argon-filled glove box with contents of oxygen and moisture below 0.1 ppm. The working electrodes were prepared by mixing the synthesized CNS and polyvinylidene fluoride (PVDF) as binder, and carbon black as a conductor with a weight ratio of 80:10:10 using n-Methyl-2-pyrrolidone (NMP) as the solvent. Then obtained slurry was coated onto a pure Cu foil (99.6%, Good fellow) and dried in a vacuum oven at 85 °C for 12 h. Lithium metal foil (Alfa Aesar) was used as a counter electrode. The liquid electrolyte used was 1 M LiPF₆ in a 1:1 v/v mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (Solvionic, France, battery grade). The charge/discharge performances were carried out on a LAND CT2001A battery system tester at various current rates in the voltage range of 0.01-3.0 V. The impedance spectra were recorded on an Autolab workstation (PGSTAT302N) by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz.

The electrochemical properties of CNS as anode were evaluated using galvanostatic charge/discharge cycles with a potential window of 0.01 - 3V. Note that the specific capacity values reported here were calculated on the basis of the CNS weight. The charge/discharge profiles of the CNS samples in the 1st, 2nd and 100th cycles at a current density of 50 mA g⁻¹ are shown in Figure 5a. The initial discharge and charge capacity of the synthesized CNS are 413 and 320 mAh g⁻¹, respectively. The initial irreversible capacity of 93 mAh g⁻¹ results from the

formation of solid electrolyte interface (SEI) film on the surface of carbon nanospheres as well as accompanied by electrolyte decomposition at a low potential region and the presence of active atoms such as nitrogen and boron [43]. After 20 cycles, the capacity is decreased to a minimum value of 300 mAh g⁻¹ as shown in Figure 5b. However, it is interesting that a gradual increase of capacity is observed from that time on. After 100 cycles, a high capacity of 360 mAh g⁻¹ is achieved. The extra capacity could arise from reversible reaction of lithium with active surface groups and dangling bonds. In addition, the long-term cycling performance and the corresponding Coulombic efficiency of the CNS at the currents of 50 mA g⁻¹ and 250 mA g⁻¹ are shown in Figure 5b. The prepared CNS as anode material demonstrate an excellent cycling stability around 270 mAh g⁻¹ and a coulombic efficiency is close to 100% over 200 cycles. To understand the good electrochemical performance of the CNS anode, the electrochemical impedance spectroscopy (EIS) was conducted (Figure 5c). By fitting the Nyquist plot with Zview software by using a two-time constant equivalent. The inserted figure 5c represent the internal resistant of the test battery system. R_f and CPE_1 are associated with the resistance and constant phase element of the SEI film. R_{ct} and CPE_2 are associated with the charge-transfer resistant and constant phase element of the electrode/electrolyte interface. Z_w is associated with the Warburg impedance corresponding to the lithium-diffusion process. in lithium ion batteries, the charge transfer resistance is a measure of the charge transfer kinetics and the charge transfer process determines the rate of transfer reaction. It can be seen that the SEI film resistance (R_f) and charge-transfer resistance (R_{ct}) of the CNS electrode are 6.0 and 70.0 Ω , respectively. The small resistances further confirm the high conductivity and the excellent cycling stability of the CNS anode.

CONCLUSION

In conclusion, we have report scalable synthesis of boron and nitrogen doped carbon based nanospheres using CVD method. As a result of characterization, it has been shown that the mesoporous CNS consist of perfectly shaped nano-sized structures which are mostly interconnected. The in-situ compression test showed that the elastic modulus of CNS structure is 33.3 GPa which is much higher than reported PS spheres, PDMS spheres, PMMA spheres and their composites with metallic nanoparticles. Additionally, we have demonstrated as an anode material for Li-ion battery application.

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Figure 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.

Figure 2. (a) Raman spectra, (b) XPS spectra, (c) FT-IR spectra of CNS, (d) thermogravimetric analysis of CNS, (e) The N_2 adsorption isotherm of spheres, (f) DFT method pore size distribution and cumulative pore volume of CNS.

Figure 3. (a, b, c) Transmission electron microscope images of $B_xC_yN_z$ spheres, it shows perfect spherical structures, (d) elemental mapping of TEM showing carbon boron and nitrogen distribution in the structure.

Figure 4. (a) Schematic showing in-situ SEM testing (b-c) Force-displacement curves extracted from nanoindentation experiments for different sized CNS structures, (d) comparison of elastic modulus of different types of nanomaterials with CNS structures.

Figure 5. (a) Galvanostatic charge-discharge curves cycled at the 1st, 2nd, and 100th cycle of CNS between 3.0 and 0.01 V at a current density of 50 mA g⁻¹, (b) Cyclic performance of the CNS electrode cycled at current densities of 50 mA g⁻¹ and 100 mA g⁻¹ (c) Nyquist plots of CNS obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range 100 kHz-0.01 Hz. The inset in (c) is the equivalent circuit used in the simulation.