Nano Bowls of Carbon by Oxidative Chopping of Carbon Nano Sphere

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Here, we report the preparation of novel carbon material having fairly uniform bowl shape in nanosize domain with varying oxygen content by a very simple oxidative chopping of carbon nanoballs, where we have effectively functionalized the inert CNS (carbon nano sphere) with carboxylate groups that can be utilized for the chemical immobilization of enzymes, bioactive compounds, and catalysts.

Porous carbon-based nanomaterials are currently receiving attention, and great progress is made to synthesize them in various shapes and sizes. Various spherical carbons nanoparticles have been fabricated using template synthesis.[1]

Recently, developed carbon nano spheres (CNSs) are interesting example of such template synthesis. The CNSs have hollow core mesoporous ball-like structures with specific surface area of ca. 1000 m^2/g and the total pore volume of ca. 0.9 cm^3/g.[2,3] Due to the large surface area and pore volume they make good material for adsorption based applications. However, chemical inertness of CNSs limits its utilization for other potential applications such as payload for bioactive compounds and homogeneous catalysts.

In this study, we report the preparation of high-oxygen-containing bowl-shaped carbon nanomaterials by controlled oxidation of CNSs. The oxidation process created numerous carboxyl groups on the bowl-shaped carbon structure that is expected to provide the required handle to support bioactive compounds and other chemicals for other applications where chemically inert and hydrophobic support are desired.

The CNSs for the present study was prepared by previous studies[2] and was characterized by elemental analysis, IR, XPS, SEM, TEM, TGA, and N_2 adsorption/desorption studies. CNSs of uniform size and shape as characterized by their SEM and TEM images were used for their oxidative chopping to create nano bowls of carbon (NBCs) with varied oxygen contents. The morphology of these bowls depends on the extent of oxidation. While lower-oxygen-containing bowls henceforth referred as NBC-1s (O; 4.30%) were as nonclustered bowls, high-oxygen-containing bowls now on designated as NBC-2s (O; 30.0%) formed aggregates arranged in a honeycomb-like architecture.

To prepare NBC-1, CNSs (1.0 g) were dispersed in acidified 50% aqueous H_2O_2 (100 mL containing 2 mL of sulfuric acid), sonicated for 5 min and then stirred at room temperature for 24 h. The oxidized material was thoroughly washed with water (till neutral pH), collected by centrifugation and dried under vacuum at 80 °C. Yield; >0.90 g after removal of lighter black particles by centrifugation. Anal. Found: C, 88.7%; H, 1.64%; O, 4.30%. IR (KBr) $\tilde{\nu}_{max}$: 1732, 1581 cm^{-1}. The lighter particles (Yield, 0.09 g) were largely very small, broken and oxidized pieces of CNSs as characterized by elemental and SEM analysis (analytical data and images are not shown here). NBC-2s were prepared by making a slurry of CNSs (1.0 g) in 0.3 M potassium persulfate solution (200 mL), which was acidified by the slow addition of concentrated sulfuric acid (30 mL). The resulting suspension was sonicated for 5 min and was heated at 60 °C under stirring for 24 h followed by stirring at room temperature for another 24 h. (Yield; 1.10 g, Anal. Found: C, 67.3%, H, 1.71%; O, 30.0%. IR (KBr) $\tilde{\nu}_{max}$: 1728, 1608 cm^{-1}. XPS showed no trace of potassium and sulfur).

The mesopores in the CNSs and oxidized CNSs were characterized by N_2 adsorption/desorption isotherm that can be classified as a type IV isotherm, according to the IUPAC.

The physical properties such as BET surface area and pore volume of NBC-1 prepared by oxidation of CNSs with H_2O_2 are quite similar to those of CNSs (Table S1).[8]

Oxidation of CNSs with acidic persulfate (sample NBC-2) caused reduction in BET surface area (956.6 m^2/g) and total pore volume (0.68 cm^2/g). Also, the pore size distribution was relatively broader where majority of pores lies in 20–50 Å with mean pore size of 30.8 Å. Notably NBC-2 also showed the presence of 133.1 m^2/g micropore area. These changes can be attributed to the oxidative chopping of CNSs to create bowl-like structure, which on agglomeration create honeycomb-like structure thereby creating micropores in-between the half-cut balls. The generation of –COOH groups along the brim of NBC-2s might have triggered agglomeration through hydrogen bonding. The presence of a peak due to the H–O–H centered at ca. 534.7 eV in XPS spectra further strengthens this conjecture.[4]

SEM image of CNSs show their regular spherical morphology. The individual balls of ca. 500 nm contained a cavity of the size ca. 360 nm with a wall of ca. 70 nm thickness. The wall thickness of the NBC-1 and NBC-2 is nearly the same. Upon oxidation these spheres were chopped into bowl-shaped materials that join together to form honeycomb-like structure in the case of high-oxygen-containing sample NBC-2 whereas in the case of relatively low-oxygen-containing material (NBC-1) the bowls were individual and not aggregated (Figures 1, S1, S2, and S3).[8]

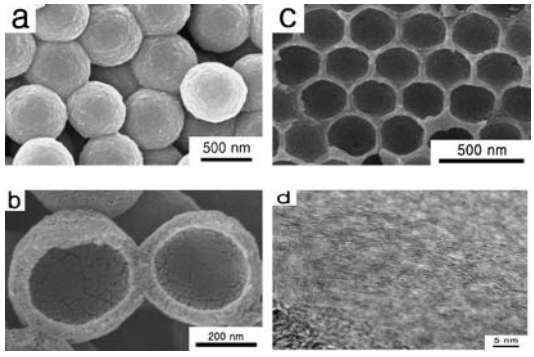

Figure 1. SEM images of (a) CNSs, (b) NBC-1s, (c) NBC-2s, and (d) HRTEM image of NBC-2s after calcination at 1300 °C under Ar showing the graphene layer.

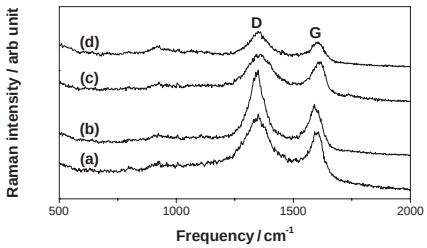

Figure 2. Raman spectra of (a) CNSs, (b) CNSs calcined at 1300 °C, (c) NBC-2s and (d) NBC-2s calcined at 1300 °C.

The possibility is that high-oxygen-containing material has more number of carboxylate groups, which might act as glue between the bowls through hydrogen bonding.

The FT-IR spectrum for CNSs in the mid IR region show distinct peak at 1589 cm^{-1} assigned to C=C stretching vibrations of aromatic carbon. A peak ≈1730 cm^{-1} appeared for the oxidized CNSs showed the presence of COOH, which is much more prominent in NBC-2 than NBC-1 sample which is in accordance with the higher oxygen content found in elemental analysis for the former (Figure S4).[8]

Due to the thickness of large-sized balls, it was not possible to see the graphitic layers however, the HRTEM image near the edge of bowls as in the case of NBC-2 (after calcination at 1300 °C under Ar atmosphere), wavy graphene layers separated by 0.30–0.35 nm, a distance close to that in graphite are clearly visible (Figure 1d).

However, in general the balls made up of more of amorphous carbon with some degree of graphitic character that increases when it was calcined at 1300 °C as evidenced by Raman spectra, which is uniquely diagnostic of many forms of carbon and was used to probe the phase of carbons synthesized in the present study.

As shown in Figure 2, the absorption at about 1580 cm^{-1} (also known as G band) has been ascribed to the Raman-active optical mode E_{2g} of 2-dimensional graphite arising out of vibrations of carbon atoms in a hexagonal carbon lattice, such as a graphene layer. Another signal at about 1340 cm^{-1} (also known as D band) is usually assigned to the vibrations of carbon atoms with dangling bonds at the end of disordered graphitic carbon. The relative intensity of the two bands (I_G/I_D) with stronger G band is an reflection of the good quality of graphite-like structure while its shifting to higher positions with higher D band intensity indicates a more disordered structure.[5] In the Raman spectra of CNSs (a) and NBC-2s (c), both the carbons gave a G band at about 1590 cm^{-1} indicating the presence of graphitic carbon in them. However, a strong D band at about 1350 cm^{-1} reveals that there are considerable structural defects in both the materials. The extent of graphitization increases as evidenced by the line sharpening and increased intensity of G band for both on calcinations of these materials at 1300 °C under Ar.

X-ray photoelectron spectra (XPS) and elemental analysis of CNSs showed that the material is largely sp^2 C=C/sp^3C–C with little amount of oxygen (Anal. Found: C, 94.2%; H, 0.47%; O, 2.27%). C1s core level peak positions of the carbon atoms are approximately at 284.8 eV, which is very close to the reported value for graphite 284.6 eV. The peak position for oxygen is centered at around 532.8 eV indicative of the presence of some O=C bonds (Figure S5).[8] Upon persulfate oxidation, there was a substantial increase in oxygen content (for NBC-2, O = 30.0%) due to the functionalization of the CNSs as it is evident from XPS spectra (Figure S6).[8] C1s peak for the functionalized CNSs shows a prominent raised bump at ≈290 eV similar to that reported in the literature largely due to the formation of –COO groups.[4] This bump is absent in virgin CNSs. Presence of strong O1s peak in the range 531–538 eV for the oxidized sample may further ratify the presence of bump in the C1s region. Relatively high percentage of hydrogen in NBC-2 sample than expected for –COOH groups alone suggest the presence of H–O–H. XPS of acid-treated carbon nanotubes[6] too show the presence of H–O–H centered at 534.7 eV.

The virgin and oxidized carbons were examined for their crystalline nature by powder XRD pattern. Both showed intense but broad Bragg reflections at ca. $2\theta = 23°$, which can be assigned to the (002) diffractions of graphite lattice ($2\theta = 26°$). Very broad peaks and lesser 2θ values are due to the higher defects and curvature of the presumably laminated structures of ball and bowl shapes of the CNSs and NBC-2s. In addition, diffractions at ca. $2\theta = 43°$ corresponding to (101) reflections of graphitic carbon were also clearly visible (Figure S7).[8] Hence, it can be concluded that carbon balls and bowls are made up of graphitic and amorphous carbon with high degree of defects caused by curvatures and porosity.[5,7] What makes the ball chopped in nearly two halves is not well understood at this point of time. The biological evaluation of these materials has shown encouraging results in the preliminary studies.

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