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Production of egg-like silica sphere in a carbon shell and their oxidation to produce egg-tray structures with high ammonia adsorption

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Abstract−A simple synthesis protocol to prepare egg-like carbon-silica hybrids was developed where the size of a silica ball housed inside a carbon shell was tunable. An egg-tray type of carbon-silica hybrid was also made by the oxidation of egg-like carbon-silica hybrids. This oxidized hybrid has shown high ammonia adsorption capacity that is about 30 times more than the standard commercial adsorbent H-ZSM-5 ($SiO_2/Al_2O_3=128$).

Key words: Carbon-silica Hybrid, Porous Material, Egg-tray Morphology, Oxidative Chopping, Catalyst Support

INTRODUCTION

Carbon and silica, both individually and in combination, play an important role in material science. Micro-/mesoporous materials are widely used as commercial adsorbents, separation materials, or catalyst supports in various fields, and as energy storage materials etc [1-3]. In such applications, the performance of the micro-/mesoporous materials is strongly influenced by their micro-/mesoporosity as well as their morphology. Therefore, the value of these materials is often decided by the regularity of their shape, size, porosity and the extent of their surface area - the higher the better. Ryoo et al., have reported the synthesis of nano-sized carbon molecular sieves (NCMS) of regular spherical shape and uniform pore distribution. Although the carbon framework of this material was highly disordered [4], it had a fairly large BET (Brunauer-Emmett-Teller) surface area (>1,300 m^2/g).

Typically, NCMS was synthesized [5,6] by the carbonization of sucrose inside the mesopores of the silica molecular sieve. The silica template was then removed by using an aqueous solution of sodium hydroxide. Similar material was also synthesized by polystyrene or phenol-formaldehyde resin coating on mesoporous silica, which was followed by carbonization and removal of silica [7].

In the present study, we report the preparation of egg-like silica sphere in a carbon shell and egg-tray structure by their controlled oxidation. The oxidation process created many carboxyl groups on carbon structure, and these materials have a potential as adsorbents and catalyst support, which was evidenced by N_2 physisorption, XPS, FT-IR, EDX and NH_3-TPD.

EXPERIMENTAL

1. Sample Preparation

For all the materials, CNBS (carbon nano ball filled with silica) was used as starting material and was synthesized according to the procedure reported by Lee et al. [8]. For the partial removal of silica, aqueous HF (hydrofluoric acid) of 5%, 8% and 10% strength was used to prepare CNBSP-5, CNBSP-8 and CNBSP-10, respectively. In a typical procedure, 100 ml of HF of appropriate strength was placed in a plastic beaker under magnetic stirring at ~400 rpm at 25 °C. 2.0 g of CNBS was placed in this stirred solution. After 30 min. of stirring, the entire mass was transferred into 1.0 liter of deionized water and the black fine powder was collected by filtration. This was then washed thoroughly with deionized water till the filtrate was of neutral pH. Finally, the material was dried in an oven at 90 °C for 24 h.

CNBSP-5 prepared by the above-mentioned method was subjected to oxidation to prepare carbon-silica hybrids oxidized. Oxidation with H_2O_2 (35% in water) and acidic $K_2S_2O_8$ resulted in almost similar oxidized materials. In a typical oxidation procedure CNBSP-5 (1.0 g) was suspended in a persulfate solution (3.0 g of $K_2S_2O_8$ in 60 ml of deionized water) and stirred magnetically for 20 min. in a round bottom flask at 25 °C. To the above stirred mass, concentrated H_2SO_4 (10 ml) was added dropwise over a period of 40 min. The reaction mixture was further allowed to stir for another 6 h, after which the entire mass was transferred into a beaker containing 800 ml of deionized water. The suspension was allowed to settle overnight and the supernatant was removed by decantation. The wet mass was washed with ~2.5 liter of deionized water until the filtrate attained neutral pH. Finally, the wet solid was taken in acetone and centrifuged at ~4,000 rpm. This removed very light and highly oxygenated carbon particles. The residue (desired material) was dried in an oven at 80 °C for 24 h.

For making smaller holes in CNBSP-5, the above procedure was used, however, the oxidation was carried out only for 1 h.

2. Sample Characterization

All the samples were characterized by SEM/EDX (Philips XL30S FEG scanning electron microscope/EDAX Phoenix Energy Dispersive X-ray Spectrometer), transmission electron microscopy (TEM, Tecnai G^2, FEI), elemental analysis (EA-1110, CE Instruments),

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X-ray photoelectron spectroscopy (XPS, ESCA-LAB MK-II (VG Scientific Ltd.)), FT-IR (Fourier transform-infrared) spectroscopy (Equinox 55 (Bruker)), and Raman spectroscopy: inverted optical microscope Axiovert 200 (Zeiss), micro objective lens 50x (Zeiss), light source of 514.5-nm Ar ion laser (Melles Griot), detector liquid-N_2-cooled CCD (Roper Scientific), and monochromator Kaiser Holospec (Kaiser Optical Systems Inc.). The crystallinity of the samples was checked by X-ray diffraction (XRD) using a Rigaku D/MAX-3B diffractometer for which Cu-Kα radiation is employed. Prior to the measurement of the isotherms at 77 K on a Micromeritics ASAP 2400 gas adsorption analyzer, the samples were degassed at 200 °C for 5 h.

For NH_3-TPD (temperature-programmed desorption) experiment, the measurement was carried out on a BEL-CAT (Model PCI-3135). All the samples were subjected to heat treatment from 30 to 100 °C for 2 h under a stream of He gas. Adsorption of ammonia was carried out at 30 °C for 1 h with NH_3 at a flow rate of 30 cc/min and the material was swept at 30 °C for 30 min with He gas at a flow rate of 30 cc/min before desorption was carried out. The desorption of ammonia was carried out over a temperature range of 30 to 1,000 °C (step: 10 °C/min.) for 30 min with He gas at a flow rate of 30 cc/min.

RESULTS AND DISCUSSION

The present study took a clue from the method of the previous studies [5,7,9,10] to synthesize new morphologies of carbon-silica hybrids by controlled dissolution of silica using aqueous HF of varied strengths. Accordingly, spherical nano balls of carbon filled with mesoporous silica (here after referred to as CNBS), were synthesized using the procedure of Lee et al. [8], as shown in Fig. 1. The partially etched carbon-silica sample (CNBSP, yolk in egg), when subjected to controlled oxidation, created a highly oxygenated carbon-silica material CNBSP-OX, having morphology akin to an egg tray. Consequently, we created a new class of carbon-silica hybrids with the hope that these novel structural motifs would find applications in diverse area where unique properties of both activated carbon and micro/mesoporous silica are readily available. It is worthwhile to note that, depending upon particular application, silica surface can be accessed readily for functionalization through mesoporous carbon shell. In our view, such motifs would be useful as catalyst support and adsorption materials. Further, the oxidized carbon-silica material (egg-tray type), as synthesized in the present study, by virtue of having carbon network with oxygenated functionalities (mostly carboxylic acid groups, IR frequency, $\nu_{C=O}$=1,719 cm^{-1}) would be handy for subsequent utilization, e.g., in catalyst and enzyme immobilization [11,12].

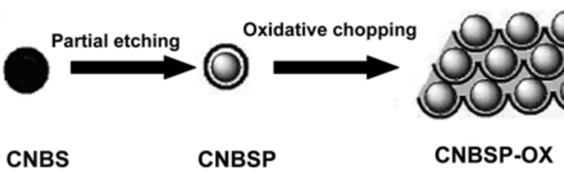


Fig. 1. Pictorial representation of carbon-silica hybrids from egg to egg-plate morphology.

The complete removal of silica from CNBS resulted in hollow core mesoporous carbon nano balls (CNB), whereas controlled etching of silica from CNBS resulted in mesoporous silica balls of variable size caged in CNB. CNB are hollow core mesoporous ball-like structures with a surface area of ca. 1,000 m^2/g and a total pore volume of ca. 0.9 cm^3/g. The individual balls of ca. 500 nm contained a cavity of diameter ca. 360 nm with a shell thickness of ca. 70 nm. The size of the silica ball can be tuned by varying the strength

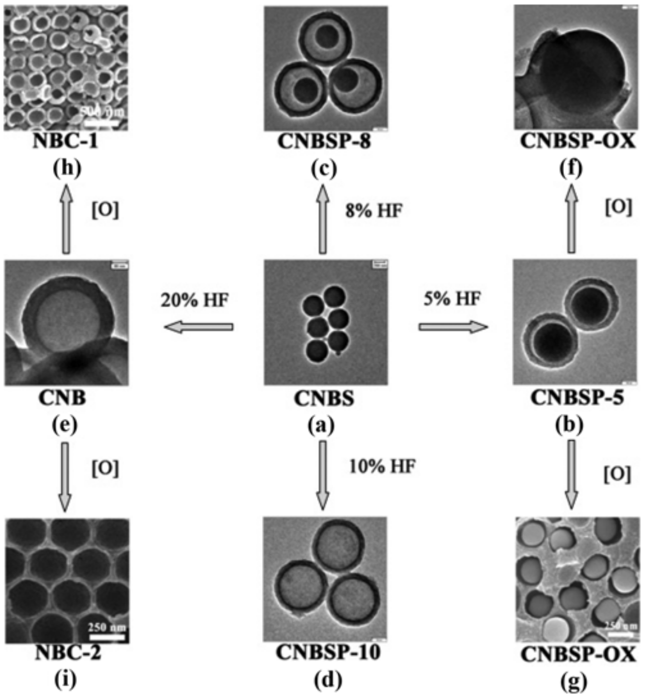
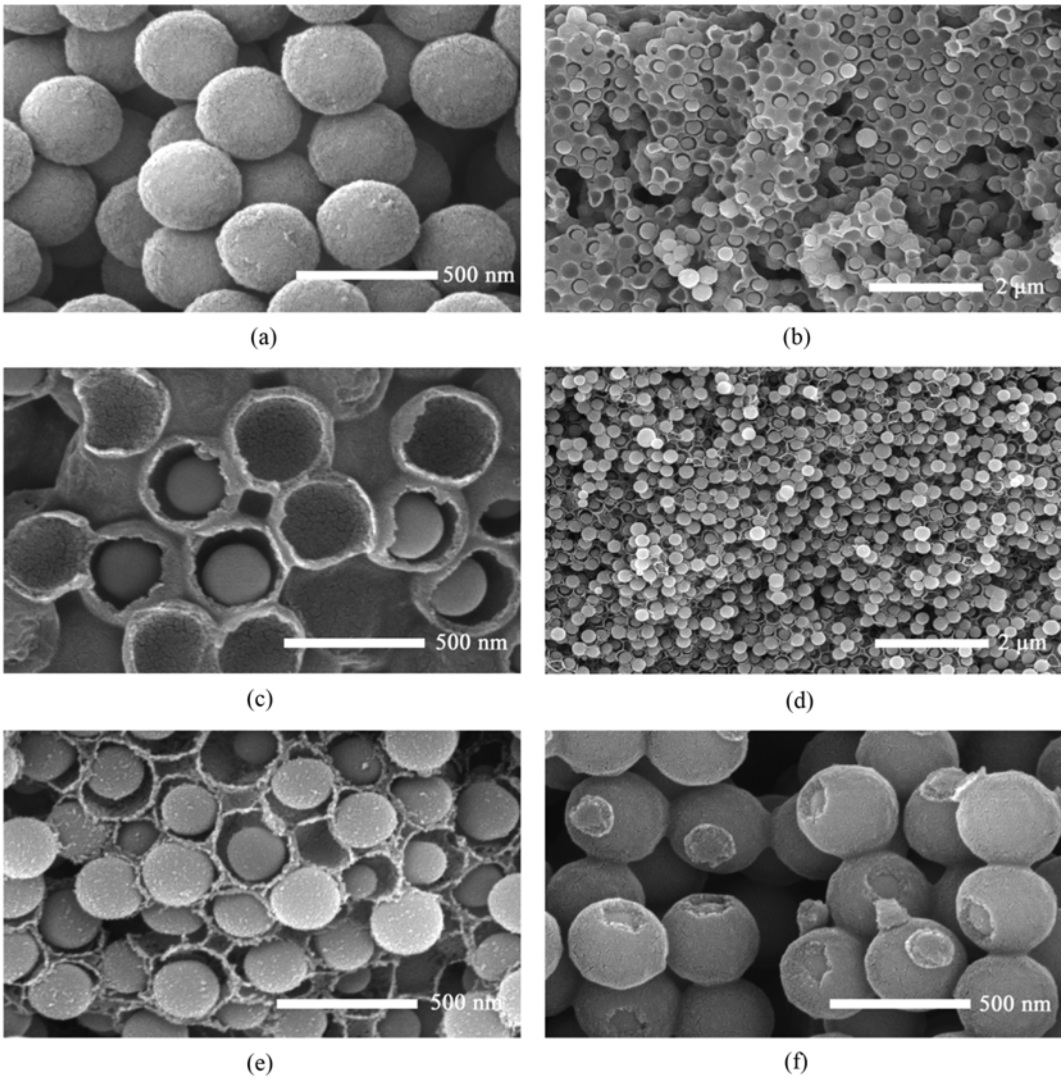


Fig. 2. From silica-filled carbon nano balls to hollow core carbon nano-balls and carbon nano-bowls. Figures (a) to (f) show TEM pictures of etching of silica at various stages by the treatment of HF. (a) silica-filled carbon nano balls (CNBS), (b) CNBS treated with 5% aqueous HF, (c) CNBS treated with 8% aqueous HF, (d) CNBS treated with 10% aqueous HF, (e) CNBS treated with aqueous 20% HF (f) CNBSP-5 oxidized with aqueous acidic $K_2S_2O_8$, (g) SEM image of CNBSP-5 oxidized with H_2O_2, (h) SEM image of nano bowls of carbon (NBC-1) and (i) SEM image of nano bowls of carbon with honeycomb like structure (NBC-2). (h) and (i) are adapted from ref. 9.

Table 1. Elemental analysis data on carbon-silica hybrids

Entry	Sample	C (%)	H (%)	N (%)	O (%)	S (%)	Residue (%)
1	CNBS	21.4	0.2	0.1	1.3	0.0	77.0
2	CNBSP-5	43.6	0.2	0.0	1.5	0.0	54.7
3	CNBSP-8	64.9	0.3	0.0	1.9	0.0	32.9
4	CNBSP-10	81.4	0.4	0.0	2.1	0.0	16.1
5	CNB	94.2	0.5	0.9	2.3	0.0	2.2
6	CNBSP-OX	33.0	0.4	0.04	6.3	0.0	60.2
7	NBC-1*	88.7	1.6	0.4	4.3	0.7	4.3
8	NBC-2*	67.3	1.7	0.6	30	0.0	0.4

*Data from ref. 9



(a) (b) (c) (d) (e) (f)

Fig. 3. SEM images of carbon-silica hybrids (a) CNBSP-5 as synthesized. (b) and (c) SEM images after oxidation with hydrogen peroxide (35%) for 24 h (d) and (e) oxidized samples after heat treatment at 1,300 °C (f) after mild oxidation depicting fairly regular-sized hole in the carbon shell through which silica ball is clearly visible.

Table 2. Surface area and pore volume data for carbon-silica hybrids

Entry	Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)
1	CNBS	56	0.06
2	CNBSP-5	558	0.55
3	CNBSP-8	863	0.72
4	CNBSP-10	1097	0.80
5	CNB	1230	1.27
6	CNBSP-OX	281	0.23
7	NBC-1*	1075	1.02
8	NBC-2*	957	0.68

*Data from ref. 9

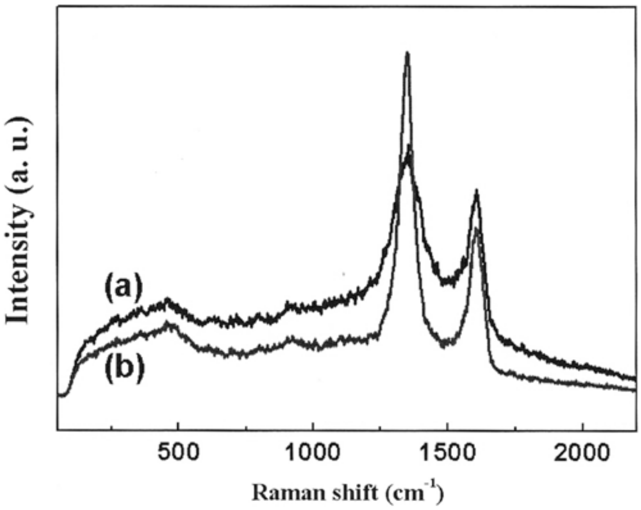


Fig. 4. Raman spectra of (a) CNBSP-OX and (b) CNBSP-OX after heat treatment at 1,300 °C under an Ar atmosphere.

of aqueous HF solution. Fig. 2 shows TEM micrographs (B to D) illustrating the various sizes of silica balls housed in CNB that were obtained from CNBS by the treatment of 5 to 10% aqueous HF.

Postscript numbers in CNBSP-5, CNBSP-8 and CNBSP-10 correspond to the strength of HF viz. 5%, 8% and 10% in water, respectively. As expected, there was a gradual decrease in the residue in elemental analysis with increase in silica etching; concomitantly there was an increase in carbon content (Table 1).

Fig. 2 represents an overall picture from silica filled carbon balls

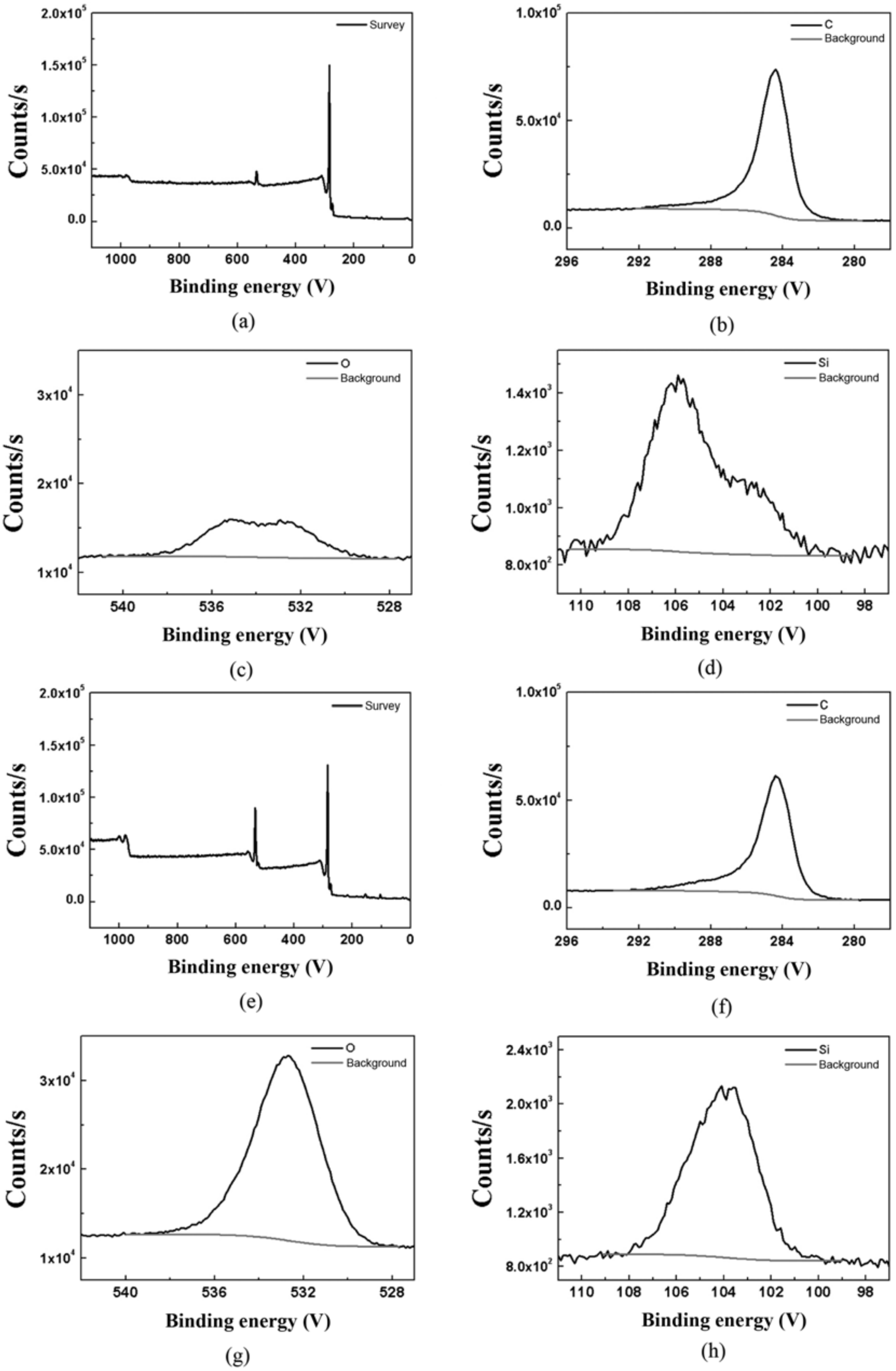


Fig. 5. X-ray photoelectron spectra (a) to (d) for CNBSP-5 and (e) to (h) for CNBSP-OX.

to hollow core carbon nano balls and carbon nano bowls.

As shown in Table 2, N_2 adsorption/desorption studies revealed that CNBS had very low surface area and pore volume as compared to the samples from which silica was partially or completely removed. Interestingly, the pore diameters for silica materials (CNBSP-5, CNBSP-8 and CNBSP-10) fall distinctly in the range of 32-37 Å, with pore volume decreasing with the decrease in silica content.

The XRD, XPS, FT-IR and EDX analysis also supported the presence of amorphous carbon and Si-O-Si groups in the synthesized materials.

Our visualization of the formation of egg-tray type morphology for the oxidation of CNBSP-5 was based on our previous experience of creating honeycomb-like structure [9] by the oxidation of CNB. This was the reason for the selection of CNBSP-5 sample with a carbon shell of diameter ~310 nm and wall thickness ~46 nm, housed with a silica ball of ~210 nm, for the controlled oxidation experiments.

Oxidation of CNBSP-5 with H_2O_2 or with acidic potassium persulfate, as per the procedure (please see experimental section), provided egg-tray kind of morphology (b and c of Fig. 3). Interestingly, it is possible to control the extent of oxidation. Hence, simply by minimizing the exposure to the oxidant, it was possible to isolate round-shaped carbon-silica hybrid material with a hole in the carbon shell (Fig. 3(f)). This morphology was intact even after its heat treatment at 1,300 °C under Ar atmosphere. The only apparent change after the heat treatment was the thinning of the carbon walls (from ~45 nm to ~20 nm) and Raman spectra in Fig. 4. In the Raman spectra, both G-band (Raman active optical mode E_{2g} for graphitic phase of carbon) at ~1,600 cm^{-1} and D-band (for dangling bonds and disorders in graphitic phase) at ~1,350 cm^{-1} became sharper. This is indicative of greater degree of graphitization of carbon after heat treatment.

The presence of oxygen in elemental analysis and XPS showed that effective oxidation had taken place. The XPS spectra from the CNBSP-OX exhibited a sub-band which was centered at 289 eV, indicating the presence of carbon due to -COOH moiety (Fig. 5(f)). This sub-band was much less pronounced in CNBSP-5. This was further verified by the presence of strong O1s band centered around 533 eV in CNBSP-OX (Fig. 5(g)) as compared to the broad and low intensity band present in CNBSP-5 in this region [13] (Fig. 5(c)). As expected in the case of CNBSP-OX, the Si 2p signal at ~104 eV, arose from the SiO_2 nanospheres (Fig. 5(h)). However, in the case of CNBSP-5, where the silica ball was completely surrounded with carbon shell, the 104 eV band was present as sub-band to ~106 eV.

The IR spectra for CNBSP and CNBSP-OX (Fig. 6) showed the presence of Si-O-Si mode at 1,090 cm^{-1}. However CNBSP-OX showed an additional band at 1,719 cm^{-1} which was assigned for -COOH ($\nu_{C=O}$) moiety created by the oxidation of carbon-silica hybrid.

Here, we have presented the ammonia adsorption/desorption studies in order to show the utility of carbon/carbon-silica as materials for ammonia storage or removal. Removal of ammonia from air is one of the many possible uses of these novel carbon and carbon-silica materials, which can be exploited commercially. H-ZSM-5 sample with ammonia adsorption capacity of 0.18 mmol/g was used as a reference material [14]. Both carbon nanoballs (without silica) and CNBSP-5 samples showed weak adsorption capacity for ammonia as compared to standard H-ZSM-5 (Table 3). Significantly, as shown in Fig. 7, upon oxidation (CNBSP-OX) the ammonia adsorption capacity of CNBSP-5 increased by more than tenfold. This is nearly 30 times more than standard sample H-ZSM-5. The desorption curve of CNBSP-OX showed a strong band below 200 °C. This suggested the presence of NH_4^+ Brønsted acid sites due to the existence of a large number of -COOH moiety on the oxidized carbon-silica hybrid. There were other desorption sites above 200 °C; however, they were of very weak intensity. This was likely due to the presence of other oxygenated carbon moieties e.g., phenol, an-

Table 3. Adsorption capacity of carbon-silica hybrid

Sample	CNB	CNBSP-5	CNBSP-OX	NBC-2	H-ZSM-5*
Adsorption (mmol/g)	1.73	0.50	5.48	23.5	0.18

*SiO_2/Al_2O_3=128, data from ref. 14

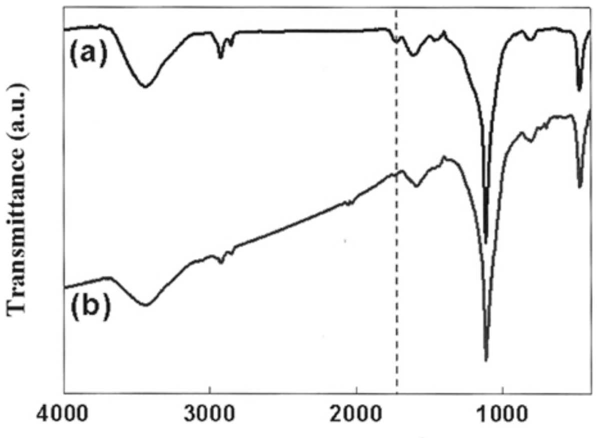


Fig. 6. The FT-IR spectra of (a) CNBSP-OX and (b) CNBSP-5. CNBSP-OX has additional band at 1,719 cm^{-1}.

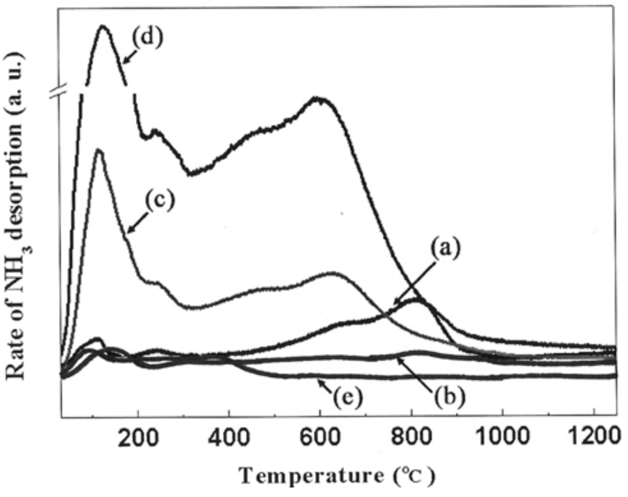


Fig. 7. The rate of desorption of ammonia over (a) CNB, (b) CNBSP-5, (c) CNBSP-OX, (d) NBC-2 and (e) H-ZSM-5 (SiO_2/Al_2O_3=128).

hydrides, ketones etc. It appears that silica contributed very little to the ammonia adsorption/desorption phenomenon in the synthesized carbon-silica hybrids.

CONCLUSIONS

The present paper describes the synthesis of egg-like carbon-silica hybrids of fairly uniform shape where the size of silica ball housed inside the carbon shell is easily controlled by the controlled etching of silica filled carbon nano balls. The oxidative chopping of carbon nano shells produced a novel carbon-silica hybrid with a fairly uniform egg-tray shape in the nanosize domain with varying oxygen content due to predominant carboxylate groups. These groups can be utilized for the chemical immobilization of active species. These materials have a potential application as adsorbent and catalyst support as exemplified by the NH_3-TPD studies.

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