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Controlling the Morphology of Resorcinol–Formaldehyde-Based Carbon Xerogels by Sol Concentration, Shearing, and Surfactants

Chandra S. Sharma, Devendra K. Upadhyay, and Ashutosh Sharma*

Department of Chemical Engineering and DST Unit on Nanosciences, Indian Institute of Technology, Kanpur-208016, U.P., India

Carbon xerogel microspheres were synthesized by inverse emulsion polymerization of resorcinol with formaldehyde, followed by pyrolysis at 900 °C under nitrogen atmosphere. We have studied the effect of various synthesis parameters, including dilution ratio and hydrophilic–lipophilic balance (HLB) of nonionic surfactants, on the size and morphology of resulting structures. The average particle size of carbon microspheres could be modulated from 1 to 28 µm by varying the dilution ratio over 3 orders of magnitude. Increase in the HLB value and the amount of surfactants produced a variety of dense carbon, but open-architecture fractal-like structures. Three different methods of stirring, namely, magnetic, mechanical, and ultrasonication were applied during the inverse emulsification to produce carbon xerogel microstructures. Formation of a wide spectrum of nonporous carbon particle morphologies, including the highly branched, hierarchical microparticles, by tuning the synthesis conditions may have potential applications in printing technology, controlled drug delivery, biosensors, and carbon-based microelectromechanical systems (C-MEMS).

Introduction
Organic gels have been a subject of interest for almost the last two decades because of their unique physical, chemical, and electrochemical properties. 1–17 Although new precursors and solvents have been used in the synthesis of carbon gels recently, 18–20 the sol–gel polycondensation route of resorcinol–formaldehyde (RF) is still the most widely used since their introduction by Pekala. 1,2 In this process, resorcinol reacts with formaldehyde under alkaline conditions in two steps. 1,9 The first step is the formation of hydroxymethyl derivatives by an addition reaction, and the next step is condensation of these derivatives to form methylene and methylene ether. 1,9 These intermediates further react to form highly cross-linked clusters of RF gel that are pyrolyzed to form carbon gels. These carbon gels are used in a variety of applications including electrode materials in rechargeable batteries and supercapacitors, etc. 2–16

The morphology of these carbon gel particles is one of the most important single factors in considering their potential for a specific application. Various kinds of morphologies in these carbon gels, for example, porous texture, microspheres, thin film, granule, and honeycomb, etc. have been reported. 1–20,21–22 Recently, dense carbon microspheres have been used as a template for the preparation of oxide hollow spheres to be used in controlled drug delivery. 21,22 There are other potential applications of dense carbon microspheres such as studying the interactions of carbon with a variety of surfaces using a microbead attached to an AFM tip. The interaction between such model particles and fabric substrates is important for detergency as it provides fundamental understanding of the forces and their manipulation to aid their removal from the surface. As reported in our recent work, 14 RF xerogel microparticles can be synthesized by inverse emulsion polymerization followed by air-drying. In this approach, RF sol is added slowly in the presence of a surfactant to form a dispersed colloidal solution. These particles were pyrolyzed at a high temperature in an inert atmosphere to obtain carbon microspheres. Sol–gel synthesis variables, method of drying, and pyrolysis conditions play a major role in determining the morphologies of carbon gels derived from the RF sol. Recently, we have shown that by tuning some of these synthesis parameters, for example, the amount of catalyst in the RF sol and the concentration of surfactant employed in the microemulsion, dense carbon structures lacking micropores but with a high external surface area resulting from their fractal-like morphology are formed. 14 Such structures may find applications in resonance-based solar cells 23 and carbon-based microelectromechanical systems (C-MEMS), including microbatteries. 14,24,25 Dense xerogels lacking micropores appear to be specially promising anode materials because intercalation of Li ions in micropores is more irreversible leading to a decline in the reversible capacity of the electrode material. Indeed, it has been shown that the reversible capacity of mesoporous carbon microbeads (MCMB) declines with an increase in its specific surface area, much of which is contributed by micro/mesopores. 25 Similar consideration also holds for aerogels. 1 Also, these microstructures have the potential to serve as a platform for cell manipulations and growth because of the biocompatibility of carbon coupled with its easy functionalization and hydrophobicity/hydrophilicity control. 26

Various method of drying may be chosen after sol–gel polymerization to obtain different levels of porosity in these carbon gels. Organic xerogels are made by removing the solvent from the gel structure by drying conventionally with nitrogen or air under normal conditions which is followed by pyrolysis to yield RF-based carbogel. These xerogels are generally dense because the capillary pressure of the liquid inside a pore leads to the collapse of the gel-network during oven drying. 9,10,14,15 However, there are few reports to synthesize the porous carbon xerogels also by changing the initial pH of the RF sol. 10–12

The specific aim of the present work is to develop a better control on the size and morphology of dense RF-derived carbon xerogel particles. We have investigated the role of diluent concentration (water in the present case) and the method of stirring, both of which affect the particle morphologies to a great extent as shown here. Other than this, choice of a surfactant with a particular HLB value to yield nonporous carbon xerogel microstructures is also studied here, which has not been discussed in literature to the best of our knowledge. Finally,
we demonstrate that nearly monodispersed, multiscale smooth nonporous carbon microspheres, as well as fractal-like branched structures may be produced by controlling these parameters. These fractal-like carbon structures are also nonporous, but have large external surface area as compared to microspheres. Hence, these highly folded, but dense carbon structures may provide larger reversible capacity and also minimize irreversible losses in lithium ion batteries compared to the electrodes made of dense carbon spheres.

The fractal structures obtained in this work are random in nature and self-similar at certain length scales. It is worth mentioning here that fractals are disordered structures described by a noninteger dimension, known as fractal dimension14,24,27 which is also presented in this study as a measure of irregularities of these structures.

Experimental Section

Materials. Resorcinol (99% purity), formaldehyde (37% w/v; stabilized by 11–14 wt % methanol) and potassium carbonate (99.0% purity) which was used as a basic catalyst were purchased from Qualigens Fine Chemicals, India, and used as such. Ultrapure milli-Q water was used as a diluent in the preparation of all samples. Organic solvent, cyclohexane (high performance liquid chromatography grade) which was used to disperse resorcinol–formaldehyde (RF) sol was supplied by E. Merck Ltd., India. A nonionic surfactant was used as an emulsifier. All three types of surfactants used in this study, Span 80 (Sorbitan monoleate, HLB value 4.3), Span 20 (Sorbitan monolaureate, HLB Value 8.6), and Tween 80 (Polyoxyethylene-sorbitan monoleate, HLB value 15) were purchased from Loba Chemie, India.

Methods. Measured quantities of resorcinol and formaldehyde were added in a beaker and mixed properly for about 15 min with the help of a magnetic stirrer. Potassium carbonate was dissolved in ultrapure milli-Q water in a separate beaker. The two solutions were then mixed and stirred continuously for 30 min until the colorless RF sol changed to golden yellow. The resorcinol to formaldehyde (RF) and resorcinol to catalyst (R/C) molar ratios were kept constant at 0.50 and 25, respectively. The dilution ratio is defined as molar ratio of resorcinol to water (R/W). It is to be noted here that water present in the formaldehyde solution is not taken into consideration while calculating this ratio. The dilution ratio was varied to 3 orders of magnitude from 0.0037 to 3.7 to study its effect on the shape and size of the droplets in dispersed colloidal solution of RF sol.

To produce RF xerogel microspheres via inverse emulsion polymerization, RF sol thus prepared was added slowly into cyclohexane in the presence of a nonionic surfactant. Continuous stirring was required during the formation of dispersed colloidal solution of aqueous RF sol. Three different methods were applied to investigate the effect of the stirring method on the size and shape of emulsion droplets. Magnetic stirring was done with the help of magnetic needles. A probe-ultrasonicator (Electrosonic Industries, India) with 10 mm probe diameter at 260 V and was used to produce sufficient agitation in the emulsion. A mechanical shaker bath (RSB-12, Remi Instruments Division, India) was another method used for stirring the emulsion.

In addition to this, the effect of nonionic surfactants with different HLB values (Span 20, Span 80, and Tween 80) was also investigated in this study. In all the experiments except those which were done to study the effect of the stirring method, magnetic stirring was used for dispersing RF sol into the oil phase.

A viscous RF sol (1 mL) was added slowly to 50 mL of cyclohexane and agitated by various methods as mentioned previously, in the presence of a nonionic surfactant. Surfactant concentration (v/v; vol of surfactant/vol of total solution) was varied from 1 to 50%. Stirring was continued from 2 to 5 h as specified case to case. Particle size could be measured by rapidly (5–30 min) desiccating the RF hydrogel particle suspension on silicon wafer used as a substrate to partially evaporate the solvent and arrest the movement of particles. Subsequently, samples were dried in subcritical conditions by heating them in an oven at 333 K for 12 h to obtain the RF xerogel particles.

After drying, silicon wafers with the RF xerogel particles were loaded in a quartz boat. This quartz boat was placed inside a high temperature tubular furnace for pyrolysis to obtain carbon particles. Before heating was started, we allowed the flow of nitrogen for 15 min inside the furnace to purge out the reacting gases present inside. After that samples were heated to 1173 K in a controlled way under constant N2 gas flow at 0.3 L/min. The furnace was programmed to reach 573 K from room temperature in 60 min with a heating rate of 4.5 K/min. At 573 K, the furnace was held at the same temperature for 30 min. After that, it reached a final temperature of 1173 K within the next 90 min (heating rate ~6.7 K/min). It was kept for 1 h at the highest temperature, and then the furnace was allowed to cool to room temperature under the flow of N2 to obtain carbon xerogel particles.

Characterization of RF Carbon Xerogel Particles. Raman spectra of individual particles to characterize the types of bonds between the elements constituting the material was recorded by a confocal micro-Raman microscope (CRM 200, WiTec, Germany with λ = 543 nm). Specific surface area of the RF carbon xerogel particles was calculated by the Brunauer Emmett and Teller (BET) method from the adsorption isotherms of nitrogen. Samples were degassed for 1 h at 393 K. The Barrett–Joiner–Halenda (BJH) method was applied to the desorption branch of the isotherms to estimate pore size distribution.

The surface roughness, size and shape of the RF carbon xerogel particles were studied using SEM (Quanta 200, FEI and SUPRA 40 VP, Gemini, Zeiss, Germany). In addition, the particles were also imaged using Samsung SDC 4304PA camera fitted to Leica Optical Microscope at different magnifications. These images were then analyzed using Leica-QWIN software (QWIN_32) to measure the particle size distribution (PSD). Two different implementations of the box counting method (fractal analysis system of NARO, Japan, and Fractalyse of TheMA Research Centre, France) were used to calculate the fractal dimension.

Results and Discussion

The chemistry of formation of the RF gel has been investigated in detail previously.1,9 Resorcinol first reacts with formaldehyde under alkaline conditions to form hydroxymethyl derivatives by an addition reaction, and then condensation of these derivatives forms methylene and methylene ether.1,9 These intermediates further react to form highly cross-linked clusters of RF gel which is finally pyrolyzed to form carbon gels.

A typical Raman spectrum of the pyrolyzed particles is shown in Figure 1. Two broad peaks centered at about 1345 and 1592 cm\(^{-1}\) corresponds to the D and G bands which show a breathing mode of rings and vibrations of sp\(^2\) carbon atoms with dangling bonds, respectively. The intensity ratio of D to G band is calculated to be 1.14, which reflects the amorphous nature of carbon structures with relatively high disorder.19
BET specific surface area of the RF carbon xerogel particles was found to be 11.91 ± 0.48 m²/g in the case of R/C = 25, span-80 concentration of 1% (v/v) and stirring time of 5 h. This is about 2 orders of magnitude smaller than the surface areas for highly porous RF carbon aerogels,¹⁻⁷ cryogels,⁸⁻¹⁰ and xerogels.¹⁻² With the increase in HLB value of the surfactant employed, specific surface area of carbon particles did not change much. For example, in the case of span-20, in which surfactant seems to have lumps of residue as discussed later, the specific surface area was found to be 45.27 ± 5.12 m²/g. The total pore volume was measured to be 0.02 and 0.06 cm³/g for span-80 and span-20, respectively, which is also quite less than the reported values for RF carbon aerogel,¹⁻⁷ cryogels,⁸⁻¹⁰ and recently reported porous xerogel¹⁰⁻¹² as well. These results show that there are no macro- or mesopores in these structures. However, the possibility of micropores which are undetectable by nitrogen cannot be ruled out. Thus, the RF-based carbon xerogel microspheres reported in our work are nearly nonporous. These dense carbon xerogel structures therefore may be a promising alternative to low surface area mesocarbon microbeads (MCMB)²⁵,²⁸ as anode materials in rechargeable batteries and supercapacitors.

Effect of Dilution Ratio. Chemistry and kinetics of the reaction between resorcinol and formaldehyde was first studied by Pekala¹ for aerogels. On the basis of that, the dilution ratio (R/W) is expected to be one of the sol–gel process variables which influences the particle morphology in xerogels. To study its effect on RF-based carbon xerogel particles, RF sol was prepared with different dilution ratios varied up to 3 orders of magnitude from 0.0037 to 3.7. R/F and R/C were fixed to be 0.5 and 25, respectively. RF sol prepared with this composition was dispersed to form a microemulsion which was continuously stirred for 5 h by magnetic stirrer.

It is observed that as the water concentration increases (decrease in R/W ratio from 3.7 to 0.0037), the gelation time of RF sol also increases widely from about 4 h to 20 days as shown in Figure 2. The increased amount of water decreases the effective catalyst concentration in the sol, and hence the rate of the polymerization reaction between the monomers slows down. Therefore, the apparent viscosity of RF sol increases gradually which means that the sol takes more time to form a cross-linked polymer (gel). This increase in gelation time and reduced viscosity before the delayed onset of gelation time allow greater opportunity for the deformation of a particle from sphere to elongated irregular shapes as shown in Figure 3a,b. Thus, it is observed that at a smaller value of dilution ratio (R/W = 0.0037), particle shape gets distorted from spherical.

The effect of dilution ratio is also observed on the RF-derived carbon particle size as summarized in Table 1. With an increase in dilution ratio (large amount of water) by 3 orders of magnitude from 0.0037 to 3.7, average size of the RF-derived carbon particles (dₐv) decreases from about 28 µm to almost 1 µm. This change of more than an order of magnitude in the particle size by changing the dilution ratio may be understood as follows. During continuous turbulent agitation in an inverse emulsification process, there are two opposite mechanisms which govern the final size of an emulsion droplet. A droplet breaks by the action of viscous shear forces and turbulent pressure fluctuations while on the other hand, drop-coalescence of randomly colliding droplets occurs which is promoted by the interdroplet turbulent and squeezing forces such as the van der Waals attractive force and the capillary pressure.⁵,²⁹⁻³¹ As also suggested by Tamon,⁵,⁶ a decrease in the dilution ratio gives larger gelation time in which the individual colloidal particles get more time to grow. This factor results in large diameter droplets at the onset of gelation.

We have not observed any significant effect of dilution ratio on the porous texture of the RF-derived carbon xerogel particles.
the periphery of the emulsion and thus generates a radial flow
chanical vibration which travels from the tip of the probe to
particles. Ultrasonication probe produces a very high me-
reduction. These results are consistent with what is known about
ing effects of ultrasonication provide a better route to size
diameter,
cation stirring as compared to magnetic stirring (average mean
observation is also made in literature for carbon aerogels. As
supported by their measured specific surface area. A similar
Figure 4.
diameter,
find that more uniform and smaller particles (average mean
in each case was 1% (v/v). On comparing Figure 4a and b, we
sonication stirring for 5 h. Surfactant (span-80) concentration
solvent and nonionic surfactant.
which RF droplets were dispersed in the presence of an organic
aggregation. Shear induced by agitation may deform and fold
these lamellas into needle-like fibrous structures shown in Figure
5a–c. These RF-derived carbon structures at supermicellar
concentration of surfactant are fractal-like in nature. The fractal
dimension of these structures is also calculated. For the
structures shown in Figure 5a–c, fractal dimension is in the
range of 1.60 ± 0.16. Moreover, we also observed that in
the case of ultrasonication, length scale of these structures is
almost 1 order of magnitude smaller than those obtained by
magnetic stirring. In the case of the mechanical shaker, shear
forces required to form the folded lamellas were apparently
sufficient. As discussed earlier, the coalescence of sol droplets
in this case produced aggregated lumps of irregularly shaped
elongated carbon structures as shown in Figure 5d.

Effect of Method of Stirring. Stirring promotes turbulence
and shear flow, which influence the dynamic equilibrium
between the two contradictory mechanisms of drop breakage
and coalescence. As stirring also governs the type of flow-field
generated in an emulsion, it is one of the important factors in
deciding the particle morphology. In the present study three
different methods, namely, magnetic stirring, probe ultrasoni-
cation, and mechanical shaker were used to stir the solution in
which RF droplets were dispersed in the presence of an organic
solvent and nonionic surfactant.

Figure 4 shows the particle size distributions of RF derived
carbon particles obtained after applying magnetic and ultra-
sonication stirring for 5 h. Surfactant (span-80) concentration
in each case was 1% (v/v). On comparing Figure 4a and b, we
find that more uniform and smaller particles (average mean
diameter, $d_{av} = 4.79 \, \mu m$) are formed in the case of ultrasoni-
cation stirring as compared to magnetic stirring (average mean
diameter, $d_{av} = 12.31 \, \mu m$). Thus, intense stirring and emulsifying
effects of ultrasonication provide a better route to size
reduction. These results are consistent with what is known about
ultrasonically induced microemulsion polymerization of latex
particles. Ultrasoundation probe produces a very high me-
chanical vibration which travels from the tip of the probe to
the periphery of the emulsion and thus generates a radial flow

as well as an axial flow field. Cavitation engendered by
ultrasonication gives rise to intense local pressure waves and
microstreaming of the liquid around the points of collapse. This
in turn leads to high shear gradients resulting in smaller size
droplets. Unlike probe-ultrasonication, a magnetic stirrer pro-
duces axial flow-field only. Higher power output in the case of
ultrasonication causes strong stirring, and thus drop breakage is
a greater dominating phenomenon in this case.

Mechanical shaking was found to be the least effective of all
the methods compared to ultrasonication or magnetic stirring.
The to-and-fro axial movement of the shaker plate was not fast
enough to prevent macro-aggregation of the emulsion even at
maximum shaking speed of 180 strokes/min. The stroke length
was 25 mm. After about 3 h of stirring, the emulsion becomes
destabilized, and macro-aggregation of the particles is observed.
The shaker was not able to vigorously agitate the emulsion and
therefore the breakup of droplets and lumps was suppressed.
Thus, RF sol droplets coalesced into lumps and settled down
in the solution.

There was no change in particles shape at lower surfactant
concentrations for the two efficient cases of stirring—magnetic
and ultrasonication. However, in the case of higher amount of
surfactant present, that is, 33% (v/v) and 50% (v/v), particle
morphology was greatly affected as shown in Figure 5. In all
the cases discussed, time of stirring was kept constant as 2 h.

At higher surfactant concentrations, lamellar phases rather
than individual micelles should be the preferred mode of
aggregation. Shear induced by agitation may deform and fold
these lamellas into needle-like fibrous structures shown in Figure
5a–c. These RF-derived carbon structures at supermicellar
concentration of surfactant are fractal-like in nature. The fractal
dimension of these structures is also calculated. For the
structures shown in Figure 5a–c, fractal dimension is in the
range of 1.60 ± 0.16. Moreover, we also observed that in
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almost 1 order of magnitude smaller than those obtained by
magnetic stirring. In the case of the mechanical shaker, shear
forces required to form the folded lamellas were apparently
not sufficient. As discussed earlier, the coalescence of sol droplets
in this case produced aggregated lumps of irregularly shaped
elongated carbon structures as shown in Figure 5d.

Effect of HLB Value of Nonionic Surfactant. Choosing
an appropriate surfactant that provides a tight control on the
size and shape of RF droplets in dispersed, colloidal solution is always important. Effectiveness of a nonionic surfactant in emulsification is correlated to its HLB value. By definition, HLB value is a measure of balance of hydrophilic to lipophilic groups present in a surfactant molecule.\(^{33,34}\) The lower the HLB value is, the more lipophilic (oil soluble) the surfactant is. Therefore, it is apparent that HLB value influences largely the stability of an emulsion and is therefore a deciding factor in controlling the morphology of RF-derived carbon particles. To study its effect, we have chosen three nonionic surfactants, namely, span-80, span-20, and tween-80. The HLB value of these surfactants is 4.3, 8.6, and 15, respectively. Span-80 and span-20 are sorbitan esters while tween 80 is its ethoxylated derivative.

In a lower surfactant concentration regime (1%, v/v), the effect of the HLB value on carbon particle morphology is shown in Figure 6. In the case of span-80 and span-20, the particles show a spherical shape. However, the surface is not as smooth for span-20 as compared to span-80. It may be because of the lumps of surfactant residue deposited on the external surface of particles for the higher HLB surfactant. Besides this, there is a decrease in average particles diameter from around 10 to 4 \(\mu m\) with an increase in HLB value from 4.3 to 8.6. As span-80 contains a bulky oleic group as compared to span-20, it causes more steric hindrance to the drop coalescence leading to a reduction in the droplet size. With the same logic, tween-80 should also produce much smaller particles. However, we observed that for the present water-in-oil system (RF sol in cyclohexane), RF sol does not get dispersed uniformly. After initial hours of stirring, macro-aggregation problem was observed because of fast destabilization of the emulsion. As shown in Figure 6c, although smaller particles are formed, they are aggregated.

On increasing the surfactant concentration to 33% (v/v), fibrous dendrite, needle-like carbon structures are obtained for span-80 and span-20 as shown in Figure 7a,b. In the case of the higher tween-80 concentration regime, some needle-like structures are formed but there is again macro-aggregation as shown in Figure 7c. Because of an unstable emulsion in the case of tween-80, the separation of the solvent phase occurred resulting in aggregation of RF clusters. The fractal dimension of the forked needle-like carbon structures obtained by using span-80 and span-20 as shown in Figure 7a,b is calculated to be 1.7 and 1.6, respectively. The branched, needle-like aggregated structures resemble “carbon flower”-type structures (Figure 5 and 7).

These fractal-like carbon structures have larger external surface area, which may provide large reversible capacity as compared to carbon microspheres with a lower external surface area. However, these carbon fractal structures are essentially nonporous lacking micro/mesopores. Thus, these structures may be useful in overcoming the problem of low reversible capacity in the lithium-ion batteries and supercapacitors arising from micro/mesoporous carbon-gels-based anode materials.

Recently, it has been shown that the fractal architecture is very favorable for an electrode to be used in lithium ion rechargeable batteries and supercapacitors.\(^{24,25}\) These branched, needle-like carbon structures may be integrated with high aspect ratio carbon structures which will lead to a manifold increase in the surface area of the carbon electrode that will enhance the lithium-ion intercalation efficiency. Biocompatibility and electrochemical properties of carbon as studied earlier\(^{26}\) enable these hybrid carbon microstructures to be used as a substrate for cell attachment and growth. Further, surface properties of these structures may be modified to enhance the differential cell adhesion\(^{26}\) and thus to achieve...
the alignment of cells on the carbon electrode. This ability may be useful in the future design of bio-MEMS.

Conclusions

RF xerogel microspheres have been synthesized by sol–gel polycondensation followed by its inverse emulsification in the presence of a nonionic surfactant. Dense carbon xerogel microspheres are obtained after pyrolysis of these RF xerogels at high temperature in the inert atmosphere. BET surface area measurement confirmed the dense nature of these carbon structures.

The effects of various synthesis parameters including the diluent concentration and method of stirring have been studied. It was found that dense, smooth spherical amorphous carbon particles with an average diameter in the range of 1–28 µm were obtained by changing the diluent ratio up to 3 orders of magnitude (0.0037 to 3.7). The shape of the particles gets distorted from spherical at very high water concentration (lower dilution ratio). In low surfactant concentration regime (1%, v/v) while ultrasonication produced smaller particles with average diameter 4.79 µm as compared to 12.31 µm for magnetic stirring, a mechanical shaker was not found to be effective at providing enough agitation. As a result, particles aggregated and settled down. At supermicellar concentration, ultrasonication as well as magnetic stirring produced large external surface area folded needle-like carbon flower type structures with fractal dimension 1.60 ± 0.16. Ultrasonication however produced similar fractal-like structures at one order smaller length-scale.

Besides these two parameters, the dilution ratio and method of stirring, the HLB value of the surfactant was also found to be effective in controlling the morphology of RF-derived dense carbon xerogel particles. With the increase in HLB value from 4.3 to 8.6, the average particles size decreased from 10 to 4 µm. However, there was no apparent change in spherical shape of these particles. External surface was found to have lumps of surfactant residue for higher HLB value surfactant. For the present system of study, tween-80 (HLB value 15.0) was not found to be appropriate as it destabilized the emulsion and phase separation occurred. A similar observation was made in the high surfactant concentration regime where span-80 and span-20 produced needle-like folded carbon bush structures with their fractal dimensions being 1.7 and 1.6, respectively.

Thus, the present methodology provides a novel route to produce not only multiscale hierarchical dense RF-derived carbon xerogel microspheres but also controls the morphology from spherical to dendritic, folded fractal-like carbon structures by tuning the various synthesis parameters. These fractal-like structures resembling “carbon flower” and “bush” have high external surface area. These structures may have potential applications depending on their morphology. We use these dense carbon microspheres of appropriate diameter as probe particles by attaching them to an AFM tip to study the interaction of surfaces with soot particles which is primarily carbon. This study is also of importance in the context of deinking of film from paper where filler particles are added to improve the printability. These dense carbon microspheres may also be used for encasing silicon powder to improve lithium ion storage capacity of silicon.\textsuperscript{15} We are also currently working toward fabricating carbon-based fractal electrode by depositing these carbon microspheres and fractal-like structures conformally on high aspect ratio carbon post arrays. Such architecture may affect the lithium intercalation properties of C-MEMS batteries dramatically. Other than C-MEMS, these fractal structures may find applications in biosensors, resonance-based solar cells, radar-adsorption materials, and thermal detectors also.

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