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In-situ hydrothermal synthesis of carbon nanorice using Nafion as a template



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ABSTRACT

Carbon nanorice has been prepared by the hydrothermal carbonization of heparin in a Nafion solution at a mild temperature of approximately 100 °C. Through transmission electron microscopy, the individual grains of this nanorice were found to have a diameter in the range of 100 nm and a length of approximately 500 nm. The mechanism of formation for this nanoscale rice-like structure is suggested to be a self-assembling process; wherein charring of the heparin causes desulfation followed by carbonization, ultimately forming 5-hydroxylmethyl furfural in the presence of a Nafion membrane. This is confirmed through Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy, with this method also shown to produce a much greater number of carbon structures than other synthesis methods. Moreover, this new method results in carbon nanorice that exhibits fluorescence, which is of great interest for potential biomedical or optoelectronic applications.

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1. Introduction

The synthesis of non-spherical nanomaterials has become vitally important in specific applications of drug delivery [1–4], as research has shown that the shape of nanoparticles used as carriers affects their biodistribution [5]. For instance, elongated organic nanoparticles have been shown to be more easily internalized into cells than their spherical counterparts with a similar volume [2]. This is especially true of the needle-like shape of nanotubes, which leads to a high internalization potential and has therefore provided a rationale for evaluating the bio-distribution of these new nanocarriers. At present, carbon nanotubes (CNTs) have been attracting considerable attention in the biomedical field, as their unique ability to penetrate cell membranes allows them to deliver therapeutic agents into the cytoplasm and, in many cases, the nucleus of

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the cell itself [6,7]. However, CNTs still present several major drawbacks, not least of which is their insolubility in most solvents [8] and need to be functionalized to be rendered hydrophilic.

Various methods have already been used to fabricate carbon nanoparticles, such as chemical vapor deposition [9], templating [10], pyrolysis of carbon sources [11], and the hydrothermal method [12]. Among these, the hydrothermal method (HTM) is one of the earliest developed techniques for the simple synthesis of water-soluble carbon materials with different aspect geometries [13]. It is also widely used due to its inherent advantages of high purity, eco-friendliness and inexpensive operation. In practice, it relies on the morphology-controlled fabrication of carbonaceous materials by one of two routine chemical pathways. The molecular precursor approach can produce various carbon nanoparticles of

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various shapes from glucose, starch/sucrose, cyclodextrins, fructose, cocoon silk and chitosan [14–19]. Conversely, the particle morphology can also be controlled by the use of a template, with hollow carbon nanoparticle (HCNP) having been achieved by using a F127 block copolymer as a template [20]. Nevertheless, most of the rod-like carbon particles that have been prepared by the hydrothermal method are in the micro scale range [21–22].

To address this shortcoming, the present study focuses on the use of heparin as a carbon source material for hydrothermal synthesis, with a Nafion template used to facilitate selfassembly. This is intended to allow for a uniform and highly reproducible particle size with an elongated rice-like shape, hereafter referred to as Nafion carbon nanorice (NCNR). Scanning electron microscopy was used to confirm the resulting morphology and dimensions; a variety of analytical techniques being subsequently utilized in determining the mechanism behind particle formation, the results of which are herein discussed.

2. Experimental procedure

2.1. Materials

Heparin sodium salt and Nafion[®] perfluorinated resin solution (5 wt% in a mixture of lower aliphatic alcohol and 45 wt% water) were purchased from Sigma–Aldrich.

2.2. Synthesis of NCNR

To synthesize NCNR, 0.5 ml of the 5 wt% Nafion solution was first added to a 25 ml round necked bottle. To this 1.1 mM of heparin dissolved in ultrapure water was added dropwise to obtain a volume ratio of Nafion to heparin of 1:5. Next, the bottle was tightly packed with paraffin for approximately 2 h without stirring. The paraffin was then removed, and the reaction was refluxed in an oil bath held at a constant temperature of 100 °C for approximately 90 min to obtain a dark blackish solid NCNR. Meanwhile, control experiments were also conducted, wherein Nafion alone was hydrothermally treated at the same ratio and temperature, but without heparin, for approximately 120 min. Heparin of the same concentration and ratio was also hydrothermally refluxed for approximately 2 h. Since no change was observed in either control experiment, it was concluded that NCNR is only obtained with Nafion acting as a template and heparin as the source material. The NCNR was obtained was dispersed in 3 ml of water, sonicated for 5 min, and then centrifuged at 16,000 rpm for 45 min prior to filtering with a 0.4 µm membrane filter. The remaining solid was dissolved in commercial methanol.

2.3. Characterization instruments

Transmission electron microscopy (TEM) images of the NCNR were obtained using a Hitachi H-7000 equipped with a CCD camera, and operating at a voltage of 100 kV. The morphology of the NCNR was assessed by scanning electron microscopy (SEM) (JEOL JSM-6390LV) and atomic force microscopy (AFM) (Bruker). X-ray diffraction (XRD) analysis was performed on a silicon wafer using a Bruker D2-phase diffractometer with CuK α radiation (λ = 1.5418Å). Change in the ultraviolet–visible (UV-VIS) absorbance of the NCNR was measured using an ultraviolet spectrometer (V670; Jasco, Tokyo, Japan), and the fluorescence of each sample was measured using a fluorescence spectrophotometer (F-7000; Hitachi). To characterize the formation of the NCNR within the Nafion membrane, Fourier transform infrared (FT-IR) spectra were recorded by a Thermo Nicolet Nexus 6700 instrument; Raman spectra were also recorded by an Andor BWII Ramarker SR-780 Newton with a 633 nm He-Ne laser as the excitation source. Thermogravimetric (TGA) data was obtained using a TA Instruments model Q500 thermo gravimetric analyzer. Finally, XPS measurements were obtained on a PHI quantera spectrometer, with the narrow scan deconvoluted using PF4 (Peak fit 4) software.

3. Results and discussions

3.1. Morphology of NCNR

The nanostructure of the NCNR was examined by TEM analysis of the charred form of heparin, as shown in Fig. 1(a) and (b); the low atomic number elements that make up the Nafion membrane making it impossible for it to be directly observed by TEM. Nevertheless, these images show that the particles produced all have a distinctive rice-like shape, with a relatively uniform length of 400–500 nm. Furthermore, the ordered structure of the NCNR exact inverse replica of the Nafion membrane swelling in the water.

This latter aspect can be explained by the fact the hydrophilic heparin is initially dispersed in the Nafion solution, and thus the water content steadily decreases over the course of hydrothermal synthesis. The self-assembly of hydrophobic components of Nafion therefore leads to a rearrangement of hydrophilic segments that ultimately creates isolated water clusters [23]. Contact between sodium ions in these isolated water clusters in turn causes charge interactions with hydrophilic heparin anions [24]; and because heparin contains a "furan structure", it has been reported that this will form carbon species during charring [25]. Further confirmation of the morphology was provided by AFM and SEM analysis, with Fig. 1(c) and (d) confirming the sub 1 μ m size of the nanorice structure produced.

3.2. Chemical composition of NCNR

Both the pure Nafion membrane and heparin aqueous solution used in this study were transparent, thus making the formation of NCNR readily apparent by a change to a dark brownish color. A more detailed analysis, however, is provided by the FT-IR spectra of Nafion, heparin and NCNR displayed in Fig. 2a. This shows that the major vibrational bands associated with both the Nafion membrane and heparin are present in the NCNR sample. The Nafion is evidenced by the C–F stretching vibrations of its polytetrafluoroethylene (PTFE) backbone that can be observed between 1100 and 1300 cm⁻¹. Similarly, the bands at 1057 and 980 cm⁻¹ are attributed to the stretching vibrations of the SO_3^- and CF_2 of Nafion, respectively [26]. The



Fig. 1 – (a–b) TEM (c) SEM and (d) AFM morphology characterisation of NCNR from heparin and Nafion by hydrothermal method. (a) Scale bar 2 μ m, (b) Scale bar 500 nm, (c) Scale bar 10 μ m and (d) 3D Scale bar 5 μ m. (A colour version of this figure can be viewed online.)



Fig. 2 – (a) FT-IR spectra of heparin, Nafion, and NCNR and (b) Raman Spectrum of NCNR. (A colour version of this figure can be viewed online.)

indicator for heparin, on the other hand, is the presence of NH, CH₂ alkyl, C=O, and SO₃⁻ at 3300, 2900, 1650, and 1057 cm⁻¹, respectively [27]. These characteristic vibrations are, however, notably weakened in the NCNR material. The decrease in the intensity of the bands at 1650 and 1057 cm⁻¹, along with the broad band at 2800–3700 cm⁻¹, suggest that dehydration occurs during hydrothermal treatment of the hybrid heparin and Nafion membrane. Moreover, the peak in NCNR at 3100– 3700 cm⁻¹ becomes broader due to the presence of residual water; and the peaks at 1710 cm⁻¹ become more pronounced due to the formation of a ketone group from the 5-hydroxylmethyl furfural during charring [28,29].

Further confirmation of the carbon structure of the synthesized NCNRs is provided by the Raman spectrum in Fig. 2b. In this, the characteristic D band peak at 1350 cm^{-1} corresponds to the disordered structure of sp² clusters, whereas the G band peak at 1579 cm^{-1} indicates the presence of aromatic and olefinic molecules coexisting with NCNR due to an in-plane bond stretching motion of C sp² atoms [30].

3.3. Crystalline structure of NCNR

In the XRD pattern for the Nafion membrane shown in Fig. 3, the peaks at 17° and 40° (corresponding to d-spacings of 5.5 and 2.4 Å, respectively) are attributed to Teflon-like domains of Nafion [31]. As the NCNR material forms, the intensity of these two peaks can be seen to drop, which indicates a progressive decrease in the crystallinity of the Nafion. Meanwhile, even though the heparin powder has no crystal lattice, we can nonetheless observe additional peaks in the NCNR at approximately 25° that strongly support the notion of a new structure [32].



Fig. 3 – XRD pattern of heparin, Nafion, and NCNR. (A colour version of this figure can be viewed online.)

3.4. Thermal properties of NCNR

From the results of the TGA analysis shown in Fig. 4, two decomposition steps are clearly evident in the thermogram of heparin. The first of these occurs in the range of 50-100 °C and is attributed to water evaporation. The second occurs in the range of 240-300 °C and can be attributed to the degradation of the saccharide structure of the molecule, which includes dehydration of the saccharide rings [33]. In the Nafion membrane, the small weight loss evident between 30 and 70 °C results from the loss of residual water within the sample [34]. However, it also exhibits a second stage degradation step at approximately 300-500 °C, with the mass loss here being attributed to the degradation of -SO₃, -C-O-Cand $-CF_2$ in the Nafion membrane [35]. In the case of the NCNR, however, the first degradation step is observed in the range of 30-220 °C; the second degradation step at 420-520 °C being attributed to the decomposition of $-CF_2$ and aromatic species formed by the hydrothermal method [36]. Moreover, the initial weight loss of NCNR at 420 °C is notably higher than the 300 °C of Nafion, which indicates that the in situ formation of carbonaceous nanorice material increases the thermal stability of Nafion. We can therefore



Fig. 4 – Thermogravimetric analysis of the heparin, Nafion, and NCNR. (A colour version of this figure can be viewed online.)

conclude that more stable oxidation of NCNR prepared at an intermediate carbonization temperature (i.e., $100 \,^{\circ}$ C) coincides with an increasing quantity of aromatic species in its carbon structure [37].

3.5. Elemental analysis of NCNR

The chemical interactions of NCNR within Nafion are further characterized by XPS, as shown in Fig 5(a-d). In the case of Nafion (Fig. 5(a)), the C1s binding energy at 286, 287, 291, 293 and 294 eV match closely with previously reported values for the β shift of sp³ carbon, -CO, -CF, -CF₂, and -CF₃[38]. In contrast, peaks for carboxylic acid at 288 eV and aromatic furan moiety at 291 eV (σ^*) are observed for heparin [39]. For NCNR and Nafion, we found that the peak at 286.7 eV was assign to carbon in an unsaturated partially fluorinated environment and we marked β shift in the Fig. 5 (a). Interestingly, the C_{1S} major binding energy of NCNR overlaps with Nafion, which indicates that the Nafion template still partially covers the surface of NCNR. Furthermore, sp2 carbon is also evident at 290 eV (σ ^{*}), with the sharp signal of the carboxylic group suggesting an aromatic fused structure such as functionalized 9-anthracene or similar organic compounds [40]. We can see from this that the Nafion not only acts as a template for heparin during hydrothermal treatment, but also as a super acid that causes charring of heparin to NCNR.

In Fig. 5(b), the O1s of NCNR shows three binding energies at 527.4 eV, 529 eV and a shoulder peak at 533.5 eV, all of which are due to the aromatic carbon atoms containing some functional group such as carbonyl, ketone, or a carboxylic compound formed during carbonization. Conversely, the O1s binding energy of heparin at 536.8 eV is attributable to a carbonyl group, whereas that of Nafion at 534.4 eV is assigned to a sulfonyl group and that at 536.8 eV represents a C—O bond.

In Fig 5(c), a C—F bond is clearly obtained in the Nafion at 695 eV, and thus we can expect that at least some of the Nafion chain is likely to form a rod structure within the carbon nanorice. Moreover, when heparin decomposes into carbon rods with Nafion at 110 °C, it is probable that the fluorine-based Nafion will covalently attach to aromatic structures in the carbon materials [41,42]. The control Nafion shows only an F1s peak at 691 eV when thermally treated without a carbon source; and since the heparin does not contain any fluorine atoms, the new peaks formed at 695 and 697 eV can be explained by the decomposition of heparin with Nafion into a new NCNR structure functionalized with fluorine [43].

In Fig. 5(d), the S2p binding energy of Nafion and heparin was 169 and 174 eV, respectively, which agrees well with previous reports [44,45]. The higher S2p energy of heparin can be explained by its sulfonic group being directly conjugated in a cyclic ring. However, NCNR does not have any sulfur atoms, which provides strong evidence that the desulfonation of heparin during hydrothermal treatment directly leads to the formation of NCNR.

3.6. Absorbance and fluorescence of NCNR

Fig. 6 depicts the UV–VIS spectrum for NCNR, Nafion and heparin in water. In the case of NCNR, there is a strong peak



Fig. 5 – XPS characterization of (a) C1s, (b) O1s for heparin, Nafion and NCNR. Fig. 5. XPS characterization of (c) F1s and (d) S2p for heparin, Nafion and NCNR. (A colour version of this figure can be viewed online.)



Fig. 6 – UV–VIS spectrum of heparin, Nafion and NCNR in water. (A colour version of this figure can be viewed online.)

centered at 275 nm that is attributed to the π - π * transition of the C=O bond [46]. This is comparable with other carbon nanoparticles, which typically have a UV-VIS absorbance in the range of 250–550 nm. From a mechanical perspective, NCNR exhibits no classic band gap absorption; and thus,

any fluorescence it exhibits should be directly related to passivated surface defects. It is possible that the Nafion may act as a surface passivation agent, as it has been reported that macromolecules covered with carbon particles can be used to stabilize surface energy traps and make the carbon particles emissive [47,48].

Fig. 7 shows the fluorescence of the NCNR when excited with different wavelengths ranging from 265 to 465 nm. At 325 nm, it clearly shows a much higher intensity of fluorescence emission, which arises due to the radioactive recombination of excitons trapped by defects in the carbon nanorice. When the excitation wavelength is increased, the fluorescence is reduced and red shifted, which is typical of carbon nanoparticles [49].

4. Conclusion

The addition of heparin has been shown to increase the water content of Nafion in an aqueous solution, thereby causing swelling of ionic clusters and ultimately leading to percolation of sodium salts of polysaccharide heparin. Subsequent decomposition and desulfation of the heparin under acidic conditions creates intermediate oligosaccharide products; which when subjected to charring, creates Nafion-



Fig. 7 – The fluorescence of NCNR in Ultra water with different excited wavelengths (265–445 nm). (A colour version of this figure can be viewed online.)



HTM – Hydrothermal Method,

Fig. 8 – The formation of NCNR by the hydrothermal method from Heparin using Nafion membrane as a template. (A colour version of this figure can be viewed online.)

encapsulated carbon nanorice (NCNR). A schematic summarizing this process is given in Fig. 8. Since this process has proven capable of fabricating large amounts of rice-like particles measuring 500 nm in length and 100 nm in diameter, and exhibiting fluorescence properties, it has great potential for biomedical and electro optical applications.

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