FLUORESCENT CARBON NANOPARTICLES FROM HYDROTHERMAL CARBON

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Introduction

Research on fluorescent semiconductor nanocrystals, known as quantum dots, has evolved over the past two decades from electronic materials science to biological applications. These materials however carry the great disadvantage of containing heavy metals, thus bringing with them potential toxicity and environmental hazardousness. Photoluminescent Carbon nanoparticles (CNPs) provide a biocompatible, low toxicity alternative to classical nanocrystals. Besides using high energy "top down" approaches such as laser ablation of a carbon precursor[1] or electrochemical exfoliation of graphite[2] so called "bottom up", wet chemical approaches have included preparation of CNPs from Candle Soot[3], Templated Silica Spheres[4] or citric acid[5]. Our group has modified the candle soot approach to synthesize CNPs, namely by using hydrothermal carbon from simple sugars as carbon precursors. The synthesis of these materials is simple, low cost and can be produced in large quantities. In combination with thermoresponsive polymer coatings these CNPs could provide a powerful tool for biomedical imaging techniques.

Fluorescent Carbon Nanoparticles - Experimental

CNP synthesis involved oxidative treatment of hydrothermally carbonized sugar (Glucose, Xylose). In a typical experiment, 20ml of a 10wt% solution of sugar in distilled water was placed in a Teflon-lined, stainless steel, 45ml volume autoclave and heated to 180°C for 16h. The resulting black precipitate was filtered and washed several times with water and dried at 80°C under vacuum overnight. The resulting black powder was calcined at 550°C for 4h under Nitrogen for further carbonization. The calcined sample was then refluxed in 30ml of 5M HNO_3 for 18h. The resulting mixture was centrifuged to remove any unreacted carbon precursor. The supernatant was neutralized using $NaHCO_3$ followed by dialysis (MWCO 100) for 2 days to remove all salts. Solid phase CNPs for elemental analysis were obtained by freeze-drying the purified CNP solution.

Results and Discussion

Hydrothermal carbon (HC) after calcination under Nitrogen (calcined hydrothermal carbon, hereafter referred to as cHC) is very similar to Candle Soot in terms of morphology and chemical composition. Candle Soot must tediously be collected, e.g. by holding a glass plate over a burning candle which realistically only gives milligrams of product. cHC however is much easier to synthesize at large scale from cheap

precursors such as carbohydrates, but also biomass agricultural wastes, and thus provides a considerably less tedious route for CNP synthesis. Fig.1 shows SEM images of Candle Soot and of Glucose-cHC. Both samples consist of spherical, interconnected particles. The only significant difference is the particle size. While Candle Soot particles are about 30nm in diameter, Glucose-cHC particles have a much larger diameter of 200nm. This however does not seem to play a role in the final result.
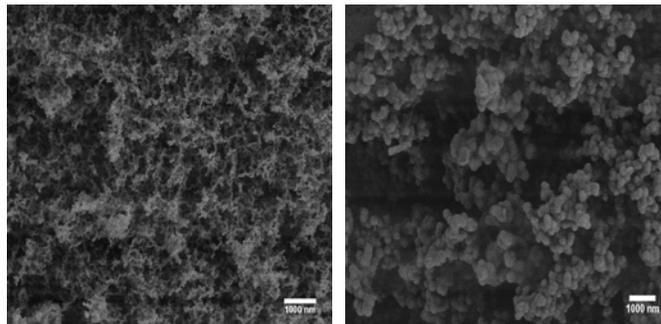
Fig. 1 SEM image showing Candle Soot (left) and Glucose-cHC (right)

Table 1 summarizes the chemical composition of different precursors and also of the CNPs derived from them. The precursors have virtually the same chemical composition and the resulting CNPs also do not vary much from each other.

**Table 1. Chemical Composition of Candle Soot and Glucose-HC**

	%C	%N	%H
Candle Soot	97,44	0,05	0,93
Glucose-cHC	96,16	0,92	2,07
Xylose-cHC	94,88	0,12	1,30
Candle Soot[3] derived CNPs	36,79	9,59	5,91
Glucose derived CNPs	36,47	4,31	2,87
Xylose derived CNPs	38,36	1,90	2,53

Fig. 2 below shows a HRTEM image of Xylose-HC derived CNPs. The spherical particles are about 2-4 nm in diameter. The absence of any discernible lattice structure indicates that the CNPs consist of amorphous carbon. This is further evidenced by the diffuse ring pattern obtained by SAED. Fig. 3 shows an FTIR spectrum comparing Xylose-HC, Xylose-cHc and solid phase Xylose derived CNPs. The stretching frequencies at ~3400cm^{-1} correspond to surface hydroxyl groups. The peak at ~1689cm^{-1} is indicative of the presence of carboxylic acid groups. The encircled region below 1700cm^{-1} is typical of HC[6] and shows the presence of a significant number of Oxygen containing groups on the surface of the

material (C=O, C=C-O, C-O-C, etc.). Interestingly, the final CNPs (green line) have virtually identical functional groups as the initial Xylose-HC before calcination (black line). Upon further carbonization the typical functional groups due to oxidation of carbohydrates disappear as the material becomes more and more carbonaceous (blue line). After HNO₃ treatment, the surface of the carbonaceous particles is re-oxidized and the same stretching frequencies reappear. It is important to note however that IR is a surface-sensitive technique and says little about the properties of the particle core. The difference between Xylose-HC and the Xylose derived CNPs is that while HC most probably has oxygen atoms incorporated throughout the material, the CNPs have an amorphous carbon core and oxygen containing surface groups. The IR spectra of both materials are thus expected to be similar.
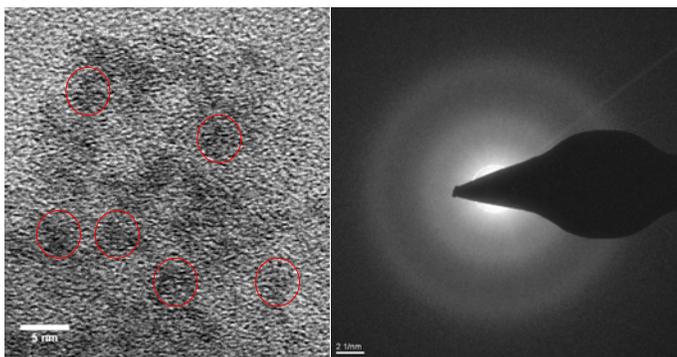

Fig. 2 HRTEM image showing CNPs derived from Xylose (left) and corresponding SAED pattern (right)
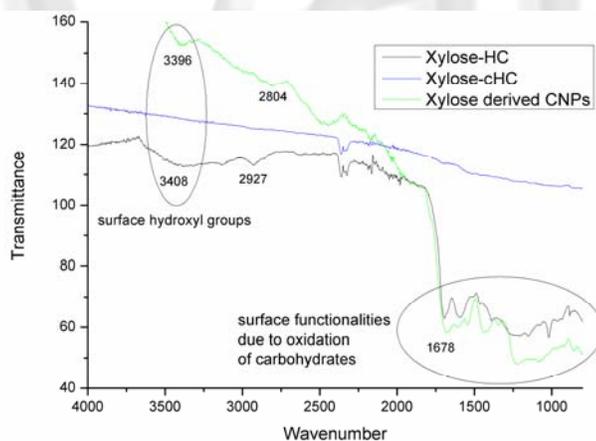
Fig. 3 FTIR spectrum of Xylose-HC (black), Xylose-cHC (blue) and Xylose derived CNPs (green).

Shown in Fig. 4 is a photoluminescence spectrum of Candle Soot derived CNPs and Xylose derived CNPs. Whilst it has not been possible to measure the exact quantum yield so far, the graph clearly shows a fluorescence peak at ~500nm. Other groups have found that surface passivation is essential for - or strongly increases fluorescence of CNPs. We have however discovered that the passivating agent commonly used, 4,7,10-trioxa-1,13-tridecanediamine (TTDDA), shows blue

fluorescence by itself after being heated to 180°C. In order to avoid artifact results we have thus opted to work with pure CNPs for the time being.
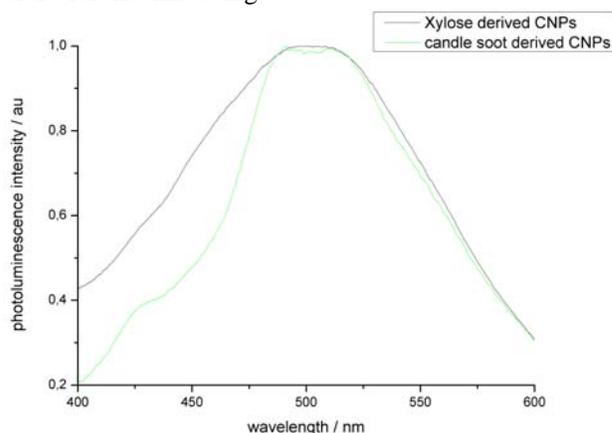
Fig. 4 Fluorescence spectrum of Xylose derived CNPs (black). A plot of Candle Soot derived CNP fluorescence is shown for comparison (green).

Conclusions and Outlook

As this abstract presents ongoing research we cannot give a final conclusion regarding the structure of the CNPs or their fluorescence mechanism. We can however say for now that hydrothermal carbon presents a viable precursor material for CNP synthesis and that results so far suggest that the CNPs produced from our material are very similar to those found in literature. Future analysis will include XRD patterns, Raman spectroscopy and Quantum Yield measurements. Once this is complete our aim is to modify the CNP surface with thermoresponsive polymers and test them for biomedical applications.

References
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