Understanding the catalytic activity of heat treated carbon nanofibres: Investigation of their dielectric properties at THz frequencies

Edward P.J. Parrott[a,b], J. Axel Zeitler[a], James McGregor[a], Shu-Pei Oei[c], Husnu Emrah Unalan[c], Swee-Ching Tan[c], William I. Milne[c], Jean-Phillipe Tessonnier[d], Robert Schlögl[d], and Lynn F. Gladden[a]

[a] Department of Chemical Engineering, University of Cambridge, Pembroke St., Cambridge CB2 3RA, U.K.
[b] Cavendish Laboratory, University of Cambridge, J. J. Thomson Ave., Cambridge CB3 0HE, U.K.
[c] Centre for Advanced Photonics and Electronics, University of Cambridge, J. J. Thomson Ave., Cambridge CB3 0FA, U.K.
[d] Fritz-Haber Institut der Max-Plank-Gessellschaft, Berlin D-14195, Germany

***Abstract*— Terahertz time-domain-spectroscopy (THz-TDS) has been used to study the electrical and optical properties of a series of carbon nanofibres (CNFs) that have undergone different heat treatments. The high temperature heat treated (HHT) sample exhibited increases in both absorption and real refractive index across the range 0.3-3.5 THz when compared to the low temperature heat treated (LHT) sample and pyrolitically stripped (PS) sample. The experimental results were fitted using a Drude-Lorentz model and an effective medium approximation to yield the electrical parameters of the sample such as the plasma frequency, phonon mode frequency and oscillator strength. These parameters were used to rationalise the differences between the samples as being due to an increased order or graphicity in the HHT sample when compared to the LHT sample, and to an even greater extent when comparing the HHT sample to the PS sample. HHT, LHT and PS CNFs can be used as catalysts for the oxidative dehydrogenation of ethylbenzene to styrene. They exhibit different catalytic activity which can be explained by their dielectric properties at THz frequencies. The results suggest that THz-TDS may become a useful tool for fundamental research into the role of electron mobility in catalyst performance.**

I. Introduction And Background

CARBON NANOTUBES (CNTs) and the more structurally complex carbon nanofibres (CNFs) have a wide range of applications, including potential uses in heterogeneous catalysis. Carbonaceous materials in catalysis are most commonly associated with catalyst deactivation, however highly ordered carbon structures have been shown to exhibit high activity and selectivity in a number of reactions The characterisation of such ordered carbonaceous materials represents a significant challenge with traditional optical spectroscopies and ^{13}C NMR spectroscopy.

CNTs have been investigated using THz-TDS in a number of previous studies.[1-5] Previous work on CNTs[2] used a combination of the Drude-Lorentz (DL) model with an effective medium approximation (EMA) to explain the differences between pristine and hydrogen-functionalised CNTs as being due to a difference in the number of available charge carriers between the two samples. In this investigation we extend this treatment to CNFs that have been heat treated at different temperatures (PS vs. LHT vs. HHT samples) and interpret their different catalytic activities in terms of the availability of charge carriers as probed using THz-TDS.

II. Results and Discussion

Figure 1 displays the frequency dependent absorption coefficient (A) and real refractive index (B) for the HHT, LHT and PS samples. Both the LHT and HHT samples show a change in both the absorption coefficient and real refractive index when compared to the PS sample, with a marked increase observed between the LHT and HHT samples. A progressively increasing gradient in the absorption coefficient is observed when comparing the PS to the LHT to the HHT sample. Similarly the refractive index of the HHT sample is markedly higher across the frequency range. The change in refractive index between the PS and LHT sample is less pronounced, but the LHT sample still appears to have a higher refractive index, especially above 1 THz.

Further understanding of the structural and electronic changes observed across the samples was made possible by modeling their dielectric response using an EMA and DL model as previously reported.[2] Two EMAs were used, the Maxwell-Garnett (MG) model and the Bruggemann (BR)

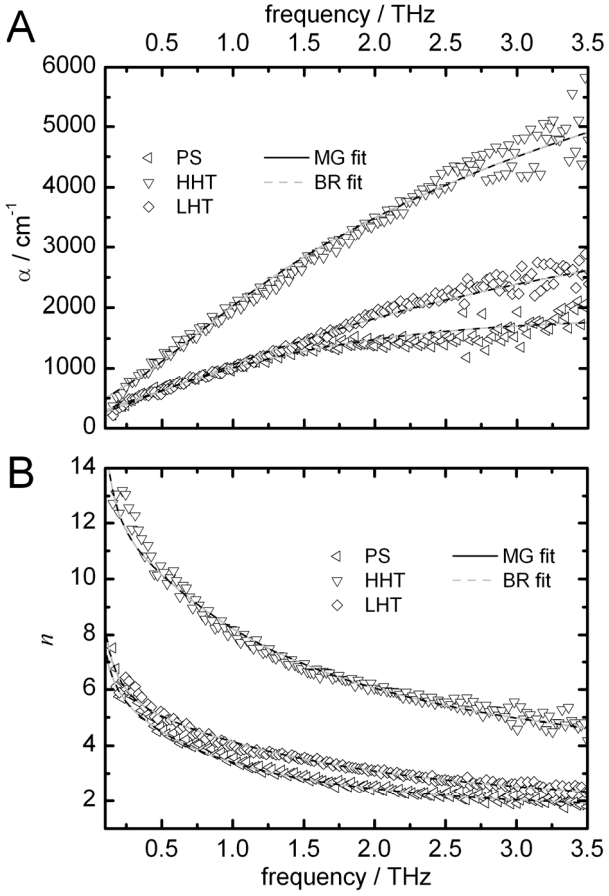

Figure 1: A) absorption coefficient and B) real refractive index for the PS, LHT and HHT samples along with the best fit MG and BR model calculations.

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TABLE 1: BEST FIT MODEL VALUES TO THE THZ DATA IN FIGURE 1. VALUES ARE IN THZ EXCEPT FOR THE LAST TWO PARAMETERS.

sample		$\Omega_p/2\pi$	$\Gamma/2\pi$	$\Omega_{p,j}/2\pi$	$\omega_{0,j}/2\pi$	$\Gamma_j/2\pi$	f	ε_∞
PS	MG	8.30	5.13	36.0	6.91	84.7	0.75	4.0
	BR	8.32	4.86	36.9	6.90	84.2	0.75	4.0
LHT	MG	16.1	16.4	36.1	6.93	48.3	0.78	2.0
	BR	16.0	14.1	39.1	7.01	49.5	0.75	2.0
HHT	MG	57.6	84.6	73.6	7.08	60.1	0.90	7.6
	BR	60.5	87.4	76.7	7.14	61.1	0.87	8.0

model, which are detailed in previous publications.[2] The best fits to these models for the three samples measured are detailed in Table 1, and their resulting dielectric responses are displayed in Figure 1.

The clearest trend observed from the data in may be found by considering the plasma frequency (Ω_p) and the Drude damping rate (Γ), where an increase in both terms is observed when going from the PS sample through the LHT sample to the HHT sample. The plasma frequency is proportional to the square root of the electron density and so an increase from 8.30 THz in the PS sample to 16.1 THz and then 57.6 THz in the LHT and HHT sample respectively is indicative of an increased number of free electrons within the higher heat treated samples when compared to the PS sample. Similarly the Drude damping rate is related to the electron collision rate[1] and so an increase in this value suggests an increase in the density of free electrons as the temperature of heat treatment increases.

The observed change in terahertz interaction with higher heating temperatures if attributed to the increased free electron availability may suggest an increased graphicity when going from the PS to the LHT to the HHT samples. This increase in order of the samples will correspondingly lead to a decrease in defect sites; it is these defect sites which may act as the catalytically active sites.

The catalytic activity of the three samples was undertaken by measuring the ratio of styrene to other hydrocarbon products produced during the oxidative dehydrogenation (ODH) of ethylbenzene (see Figure 2). The ratios after eight hours on stream were 16, 5.6 and 2.0 for PS, LHT and HHT samples respectively. The higher ratio of styrene is indicative of an increased catalytic activity and so the trend in activity of the three samples is in agreement with that measured using THz-TDS, if the defect sites are indeed related to catalyst activity.

III. CONCLUSIONS

We have reported on the application of THz-TDS in understanding the measured catalytic activity of CNFs heat treated at different temperatures. An observed decrease in catalytic activity with CNF heat treatment temperature was characterized as being due to an increase in the graphicity in the sample causing loss of defect sites which are important as reaction sites for the ODH mechanism. The observed changes in the terahertz response were rationalized by employing the DL model and an EMA, where it was indicated through an increase in the plasma frequency and Drude damping rate that

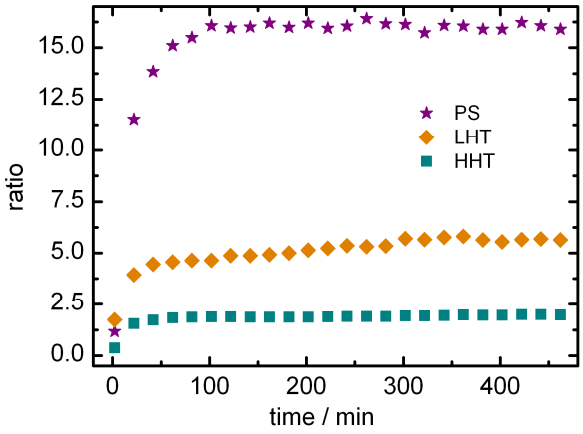

Figure 2: Styrene yield ratio as a function of time on stream for the PS, LHT and HHT sample giving an indication of the catalytic activity of the three samples.

the HHT sample, and to a lesser extent the LHT sample, had a higher mobile electron density and a more substantial region of graphene-type order, therefore fewer defect sites, when compared to the PS sample. The sensitivity of THz-TDS to changes in the conductive properties of such graphitic structures makes it an ideal tool to understand the physical and electronic properties of these materials, which cannot be studied by traditional approaches such as NMR due to the increasing conductivity of the sample.

REFERENCES

[1] T. I. Jeon, J. H. Son, K. H. An, Y. H. Lee, and Y. S. Lee, "Terahertz absorption and dispersion of fluorine-doped single-walled carbon nanotube," *J. Appl. Phys.*, vol. 98, no. 3, p. 034316, 2005.

[2] C. Kang, I. H. Maeng, S. J. Oh, S. C. Lim, K. H. An, Y. H. Lee, and J. H. Son, "Terahertz optical and electrical properties of hydrogen-functionalized carbon nanotubes," *Phys. Rev. B: Condens. Matter*, vol. 75, no. 8, p. 085410, 2007.

[3] I. Maeng, C. Kang, S. J. Oh, J. H. Son, K. H. An, and Y. H. Lee, "Terahertz electrical and optical characteristics of double-walled carbon nanotubes and their comparison with single-walled carbon nanotubes," *Appl. Phys. Lett.*, vol. 90, p. 051914, 2007.

[4] H. Nishimura, N. Minami, and R. Shimano, "Dielectric properties of single-walled carbon nanotubes in the terahertz frequency range," *Appl. Phys. Lett.*, vol. 91, p. 011108, 2007.

[5] R. Rungsawang, V. G. Geethamma, E. P. J. Parrott, D. A. Ritchie, and E. M. Terentjev, "Terahertz spectroscopy of carbon nanotubes embedded in a deformable rubber," *J. Appl. Phys.*, vol. 103, no. 12, p. 123503, 2008.

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