Hydrogen dynamics in HiPco carbon nanotubes

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Abstract

Anelastic spectroscopy experiments in HiPco carbon nanotubes from room temperature to 3 K displayed a thermally activated relaxation process at about 25 K for frequencies in the kHz range. The activation energy obtained by the peak shift with frequency is $E_a = 635$ K and reveals the presence of a very mobile species performing about 10^3 jumps/s at the peak temperature. The derived value of the pre-exponential factor of the Arrhenius law for the relaxation time, $\tau_0 = 10^{-14}$ s, is typical of point defect relaxation and suggests that the process is originated by the dynamics of hydrogen or H complexes. The peak is much broader than a single Debye-relaxation process, indicating the presence of intense elastic interactions in the highly disordered bundle structure. There are clear, but not conclusive, indications that the relaxation process is governed by a quantum mechanism.
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1. Introduction

Carbon nanotubes (CNT) have attracted much interest in the field of hydrogen storage, as high hydrogen adsorption values ranging between 0.4 and 67 mass% (for a review, see Refs. [1–4]) have been reported. Despite the fact that the more recent literature seems to indicate that the highest values reported previously are due to experimental artifacts, carbon nanotubes still need to be investigated to understand their adsorption mechanisms and properties, especially, from a fundamental point of view. To our knowledge, there are only a few reports on the diffusion of H adsorbed on single-walled carbon nanotubes [5] and on the kinetics of H [6]. In this paper, we report the first experimental observation and analysis of relaxation processes associated with the dynamics of hydrogen in single-walled HiPco nanotubes.

2. Experimental

HiPco single-walled carbon nanotubes were purchased from Carbon Nanotechnologies Inc. The material containing about 5% of Fe was suspended in a 1% water solution of sodiumdodecylsulphate and was filtrated, producing pieces of bucky paper. Two samples 1 and 2 were prepared with the form of prismatic bars of about 38 mm × 6 mm × 0.1 mm. A SEM image of the bucky paper samples is reported in Fig. 1. Sample 1 was measured starting from the as-received state, whereas sample 2, after preparation and before the measurements, was heated for 1 h at 500 K in order to remove water and subsequently was hydrogenated at a pressure of 72 bar.

For the anelastic spectroscopy measurements, the samples of bucky paper were suspended on their nodal lines and electrostatically excited in more than one of their vibration modes by a frequency modulation technique, in order to measure the complex elastic modulus $M(\omega) = M'(\omega) + iM''(\omega)$ at various frequencies and as a function of temperature. The dynamic Young modulus $M'(\omega)$ was obtained from the vibration frequency according to the relation $\omega/2\pi \propto \sqrt{M'}$, while

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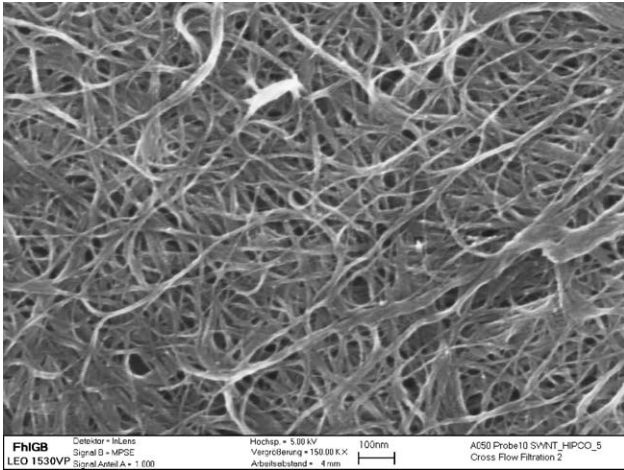Fig. 1. SEM image of a typical sample of bucky paper.

the elastic energy dissipation coefficient (or reciprocal of the mechanical Q), given by $Q^{-1} = M''/M'$ [7], was measured by the amplitude decay of the free oscillations or by the width of the resonance curve.

3. Results and discussion

Fig. 2 shows the elastic energy dissipation curves of samples 1 and 2 after various treatments. The dissipation of the as-received sample 1 as a function of temperature (curve 1) displays a peak centred at about 25 K at 356 Hz. A thermal treatment at 600 K in vacuum for 19 h produces a marked increase of the peak height (curve 2), but after a subsequent treatment in vacuum at 700 K for the same time the peak height is substantially reduced (curve 3). The dissipation curve of sample 2 after hydrogenation at 72 bar is reported in same Fig. 2 (curve 4). It can be seen that the peak is nearly totally depressed, but after a subsequent thermal
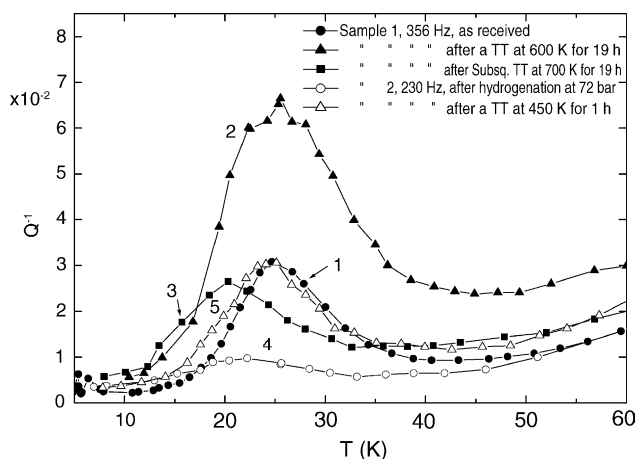

Fig. 2. The elastic energy loss spectrum of: (i) sample 1 in the as-prepared state and after two subsequent thermal treatments at 600 K for 19 h and at 700 K for 19 h and (ii) sample 2 hydrogenated at 72 bar, before and after a thermal treatment at 450 K for 1 h.

treatment (450 K for 1 h), the peak is well developed (curve 5). It is noted that both samples display a slight peak shift to higher temperature when their height increases after the thermal treatments.

The dissipation curve of sample 1 in the as-received state (curve 1 in Fig. 2) is reported in Fig. 3 together with the curve of a higher vibration mode (2060 Hz). The peak shift towards higher temperature with the frequency increase demonstrates that the peak is originated by a thermally activated relaxation process. It means that there exists a very mobile species in the sample which performs about 10^3 jumps/s at 25 K. Assuming the classical Arrhenius law for the relaxation time $\tau = \tau_0 e^{E_a/kT}$, the following values of the activation energy for the jumping process and the pre-exponential factor were obtained: $E_a = 635$ K, $\tau_0 = 10^{-14}$ s.

The drastic effect on the peak height of both the H charge (curve 4 of Fig. 2) and the H evolution out of the samples after the thermal treatments in vacuum (curves 2, 3, 5) strongly suggest that the observed relaxation process is due to hydrogen dynamics. Moreover, as the value of the prefactor is typical of point defect relaxation, it can be inferred that hydrogen or complexes containing H are involved and that they are very mobile in single-walled carbon nanotubes. It cannot be established at present whether the observed H dynamics is caused by local motion or by long-range diffusion. However, the high temperatures required for H outgassing (considering that there are no surface barriers as in the bulky samples) suggest a local reorientation mechanism, possibly around impurities or structural defects acting as firm trapping centres for H.

The presence of the peak also in the as-received sample (curve 1 of Fig. 2) suggests that hydrogen is present in carbon nanotubes as an impurity, even when they are non-intentionally exposed to H_2 atmospheres. In fact, hydrogen may be included in the bucky paper structure during the preparation procedure or by the treatments with strong acids like HCl or H_2SO_4 used to remove part of the Fe nanoparticles which act as catalysts in the HiPco procedure used to grow the carbon nanotubes. Indeed hydrogen contamination
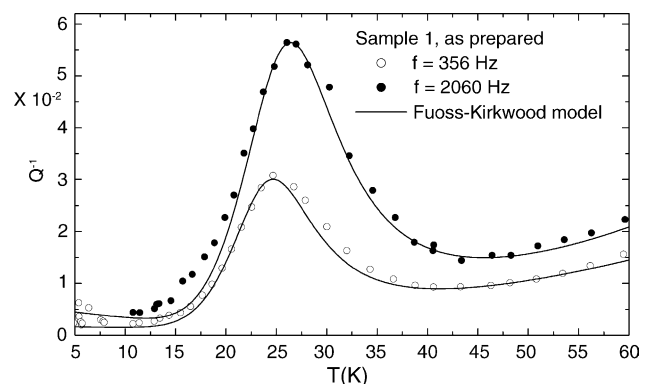

Fig. 3. Experimental data of the observed relaxation peak in sample 1 at two frequencies in the as-prepared state (symbols). The continuous lines are the best-fit curves obtained by means of the Fuoss–Kirkwood model.

during the growth process is well known for semiconductors [8]. The increase of the peak height with the H outgassing that accompanies the thermal treatments (curves 1, 2, 4 and 5) might be interpreted with an unblocking mechanism. Precisely, the H dynamics would be blocked at high concentrations, as H needs unoccupied neighbouring interstitial sites for reorientation around the trapping centres. With proceeding H outgassing, progressively more sites are made available for H jumps and hence more complexes can relax and contribute to the peak height. The decrease of the peak height with further thermal treatments (curve 3) is explained with the H depletion of the sample. The increase of the peak temperature on decreasing H content can be explained assuming a distribution of the H site energies in the highly disordered CNT structure. At low concentrations, H occupies the deeper sites and the corresponding higher activation energies for reorientation place the peak at higher temperature (at a fixed frequency). With increasing c_H, sites of progressively higher energy are filled by H, requiring a lower activation energy for reorientation. A detailed statistical model interpreting the relaxation and trapping of interstitials by substitutional atoms in solids was published elsewhere [9]. The shift of the peak at the residual H contents need further experiments and will not be discussed here.

The features of the presently reported relaxation peak might also be explained assuming that the mobile species causing the peak is different from hydrogen and that H blocks its dynamics. A high local mobility might be possible for (even heavy) atoms residing in multi-well potentials separated by a low barrier. In this case, however, the drop of the peak height with severe H outgassing would not be understood.

In order to have quantitative information about the observed relaxation process, we tried to fit it by a single-time Debye curve [7]:

$$Q^{-1} = \frac{Mv_0(\lambda_1 - \lambda_2)^2 n_1 n_2}{T} \frac{1}{(\omega\tau)^\alpha + (\omega\tau)^{-\alpha}} \quad (1)$$

where M is the Young modulus, v_0 the unit cell volume, c the molar concentration of defects which can relax between two states (1 and 2), λ_1 and λ_2 the elastic dipoles of the defects in their two configurations, n_1 and n_2 the fractions of defects in each state, $\omega = 2\pi f$, with f the vibration frequency of the sample, τ the relaxation time and $\alpha = 1$. The experimental curves resulted to be markedly broader than a single Debye peak, and this implies a distribution of the relaxation parameters (E_a and τ_0), which is generally caused by elastic interactions, as would be expected in a highly disordered system like the present one. To obtain a quantitative evaluation of the broadening we adopted the Fuoss–Kirkwood fitting procedure, which allows α to assume values lower than 1; in this case, the peak width at half height is larger than a Debye peak a by a factor α^{-1} [7]. By fixing the values of E_a and τ_0 obtained from the peak shift with frequency, the best fitting value for α, after subtraction of the background

dissipation by a parabolic law, resulted to be 0.26 (continuous line in Fig. 3). This strong deviation of the Fuoss–Kirkwood parameter from the unity and the impossibility to fit the data from both frequencies with a unique value of the relaxation strength (the prefactor in equation [1]), rise serious doubts that the observed process can be described by the classical hopping expressed by the Arrhenius law for τ.

Unfortunately, a conclusion on the regime governing the observed process cannot be drawn before carrying out new experiments, for instance on the isotope effect. In fact, a coherent tunnelling mechanism, for instance a two-level system, would give curves much broader than the observed ones for electron or one-phonon transitions (nearly linear dependence of τ^{-1} on T) and much narrower curves for multiphonon transitions (power law temperature dependence of τ^{-1}). On the other hand, considering incoherent tunnelling, which would be more likely operative at those relatively high temperatures, the only expressions for the relaxation rate of the hopping particle in terms of physically visible parameters were given by Flynn and Stoneham [10], and successfully applied to the H motion in Nb [11]. According to that model, the dependence of τ^{-1} is exponential at temperatures higher than the Debye temperature θ_D and is proportional to T^7 at temperatures lower than θ_D. It means that also in the quantum mechanical cases a very broad distribution is required to fit our data. Therefore, additional experiments should be done in order to discriminate the regime governing the observed relaxation process.

4. Conclusions

By means of anelastic spectroscopy, we report the first evidence of the existence of a mobile species characterized by a fast dynamics in HiPco carbon nanotubes. The sequence of experiments strongly suggests that hydrogen or complexes containing H are directly involved in the mechanism giving rise to the relaxation process observed. In addition, our measurements point out that hydrogen is present in nanotubes even if they are not intentionally exposed to H_2 atmospheres. The analysis of the elastic energy dissipation curve as a function of temperature reveals the presence of strong elastic interactions with the mobile entities and indicates that the H dynamics is hardly governed by a classical mechanism, but a conclusive assertion requires additional experiments.

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