

POSITRON LIFETIME AND COINCIDENCE DOPPLER BROADENING STUDIES OF GRAPHENE OXIDE – POLYANILINE NANOCOMPOSITE

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ABSTRACT

In this work, we report about the results of a detailed investigation comprising of measurements of positron lifetimes and coincidence Doppler broadening of the electron-positron annihilation gamma ray spectra on graphene oxide – polyaniline nanocomposite samples prepared with different ratios of weight and at different temperatures. The two experimental techniques are capable of providing information respectively on the electron density and momentum distribution at the specific sites of annihilation. This makes them effective in identifying the different types of defects present in the composite matrix. The magnitudes of the positron lifetimes were commensurate with the expectation of very large size defects in the form of vacancy clusters within the atomic composition of the composite material. The average defect size apparently reduced when the relative abundance of polyaniline increased that led to increased reduction of graphene oxide to graphene. The reduction also resulted in the shrinkage of the graphene oxide matrix and the free volume thereby released added to the overall defect concentration. The variation of the positron lifetime and its intensity with the temperature of synthesis suggested an optimum temperature suitable for the process.

Keywords : graphene, polyaniline, defects, vacancy clusters, positron annihilation, nanocomposites.

INTRODUCTION

Graphene, the enchanting monolayer of graphite, is fast growing as a material of great scientific importance due to the high promises it holds for technological applications [1, 2]. Research using a number of experimental techniques is rapidly progressing with a view to explore its many versatilities and many of these studies have already poured in very exciting information on its structural aspects and remarkable properties.

With a single monolayer composition and the necessity to have atomic arrangement as perfect as possible, it is often required to detect and characterize the structural defects in the graphene or graphene-related systems with preci-

sion and accuracy. Positron annihilation is the best option as it has the potential to reflect the electronic environment around vacancy-type defects through measurable changes in the energy and momentum of the annihilation gamma rays [3]. The lifetime of a positron emitted from a radioactive source (say, for example, ^{22}Na) and simultaneously entering into a material medium is related to the density of electrons through the relation

$$\tau = (\pi r_0^2 c \xi n_e)^{-1} \quad (1)$$

where r_0 is the classical electron radius, c is the velocity of light and n_e is the electron density at the site of annihilation. ξ accounts for the local enhancement in the electron density due to Coulomb interaction between the positron and the neighbouring electrons before it eventually gets annihilated by one of them.

The gamma rays resulting from electron-positron annihilation normally experiences Doppler shift due to the momentum of the electron and hence the 511 keV gamma ray spectrum recorded using a high pure Ge detector will suffer from broadening and the lineshape of the spectrum will represent the electron momentum distribution in the material [3].

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

Graphene oxide (GO), bearing oxygen functional groups on the basal planes and edges of graphene, have been used for the preparation of graphene oxide – polyaniline (PANI) composite with different relative abundances. The weight of PANI was fixed as 102 mg and graphene oxide in different amounts, viz., 51, 26, 10.2, 5.1 and 1 mg, were used for preparing samples of the different compositions. The relative abundance (x) is calculated as the percentage by weight of PANI. Thus, five samples with $x = 66.7, 80, 90.9, 95.2$ and 99% were prepared in one set. The reaction temperature had been 268K. In another set, samples with $x = 90.9\%$ were prepared at three more different temperatures, viz., 283, 298 and 313K. All the samples were studied using different experimental techniques such as electrochemical analysis, x-ray diffraction and Raman spectroscopy. For positron annihilation measurements, a ^{22}Na radioactive source taken within a ultra-thin Ni foil was sandwiched by the sample sheets. The sandwich as a whole was further sandwiched by two Si pellets to prevent the positrons from escaping into air. To prevent moisture condensation and gas absorption, the sandwich as a whole was kept under vacuum ($\sim 10^{-3}$ mbar) while data were acquired for prolonged intervals of time. Positron lifetime measurements were done using a gamma-gamma coincidence spectrometer with prompt time resolution (full width at half maximum) 180 ps. The contributions from the source material ($^{22}\text{NaCl}$), the supporting foil (Ni) and the backing Si samples were carefully estimated and removed before the spectrum were

analyzed for the different positron lifetimes in the sample [4]. Coincidence Doppler broadening measurements were carried out using two high pure Ge detectors with resolution 1.2 keV at 511 keV [5].

RESULTS AND DISCUSSION

The positron lifetime spectra due to annihilations taking place within the graphene oxide – PANI nanocomposite samples gave two lifetimes τ_1 and τ_2 (with relative intensities I_1 and I_2) in which the latter is a true representation of the nature and size of the predominant positron trapping site present in the sample. The first component τ_1 is described in positron literature as an admixture of the bulk positron lifetime (τ_b) and the Bloch state residence time (τ_b), as a result of which $\tau_1 < \tau_b$. Since an ideal sample with absolutely no defects in it even in trace amounts is difficult to achieve, an estimate of τ_b can be obtained from the trapping model equation [3]

$$\tau_b = \frac{\tau_1 \tau_2}{\tau_1 I_2 + \tau_2 I_1} \quad (2)$$

Initially a sample was prepared by reducing the graphene oxide to graphene and then using it to make the composite with PANI. In this case, we obtained $\tau_1 = 63$ ps and $\tau_2 = 402$ ps (with relative intensities $I_1 = 30.9\%$ and $I_2 = 69.1\%$). Using the above equation (2), we get $\tau_b = 151$ ps. Although this is lower than that for crystalline graphite (215-225 ps [6]), it is consistent with that obtained in a similar way for multi-wall carbon nanotube-embedded polyacrylonitrile samples [7]. More important is the presence of a very large defect-characteristic lifetime τ_2 of 402 ps with a large intensity $I_2 = 69.1\%$. This indicates a high defect concentration of the vacancy cluster-type within the composite.

As the relative abundance of PANI increased, τ_2 got reduced, as shown in *fig. 1a*. The positron lifetime in pure PANI has been reported as between 360-380 ps [8]. The combined positron lifetime will decrease with increasing percentage of PANI. What is noteworthy is an enhancement in I_2 (*fig. 1*), which is not unexpected since PANI itself is of a structure that has rich concentration of free volume defects associated with it. With increasing abundance of PANI, more positrons may get trapped in these defects. Further that PANI has the ability to reduce graphene oxide to graphene also contributes to shrinkage in the occupied volume whereby free volume cavities are generated within the PANI matrix. Both these factors must have resulted in the increase in I_2 .

It may be mentioned that a third positron lifetime τ_3 ($\sim 2 - 5$ ns) also resulted in the analysis. This was attributable to the formation of positronium atoms, which are metastable bound states of one electron and positron each [3]. This happens within the free volume defects in PANI but, since the intensities of this component were negligibly small ($< 1\%$), it is not further discussed.

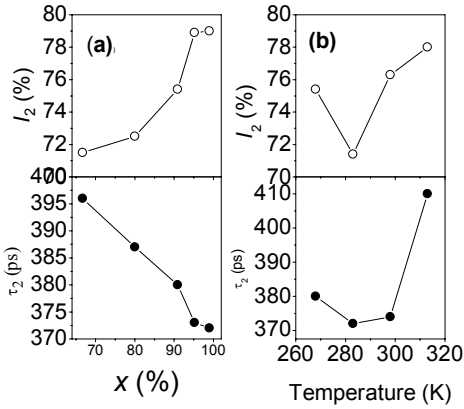


Fig. 1 – (a) The defect-characteristic positron lifetime τ_2 and its intensity I_2 versus x . (b) The variations of the two parameters with sample preparation temperature.

The coincidence Doppler broadening measurements help to suggest the relative variation in the annihilation of positrons with electrons of different elements present in a sample matrix. *Fig. 2* shows the characteristic peak of annihilation with carbon electrons. The peaks appear at an electron momentum $p_L = 9.8 \times 10^{-3} m_0 c$ (m_0 is the electron mass) whereas the intensities of the peaks display variations with samples changing their PANI abundance (x).

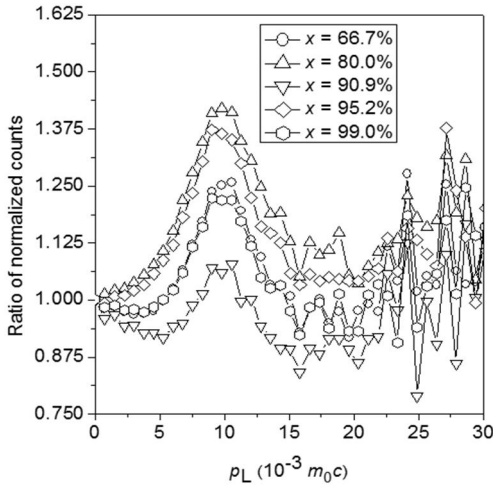


Fig. 2 – The ratio curves obtained from coincidence Doppler broadening spectra of some of the samples.

Finally, we also performed measurements in a few samples with fixed x ($= 90.9\%$) but synthesized at different temperatures. In this case, we found an initial decrease followed by a substantial increase in both the lifetime τ_2 and intensity I_2 (Fig. 2). While the temperature helps in migrating and condensing isolated smaller vacancies with the existing larger vacancy clusters, thereby directly enhancing the value of the positron lifetime, the corresponding rise in I_2 is incomprehensible as it points towards the production of additional defects. These and additional details are currently under serious consideration and need better understanding through advanced measurements and analysis.

CONCLUSIONS

Positron annihilation spectroscopy is rather unusual but innovative for novel material systems. In one of the very few attempts made so far to study graphene systems using defect spectroscopic techniques, we report in this paper the results of conventional positron lifetime measurements in graphene oxide – PANI composite to understand the types of defects inherently built in it. Notwithstanding the controlled experimental conditions including ambient temperatures used in the preparation, we observed very large lifetimes for positrons injected into the samples indicating the presence of void-like cavities. With increasing abundance of PANI in the nanocomposite, there is a distinct reduction of positron lifetime and the generation of additional defects. It indicates the shrinkage when graphene oxide is successfully reduced to graphene by the reducing agent. The observations also call for more stringent methods of experimentation while synthesizing such samples for spectroscopic investigation. The variation arising from difference in sample preparation temperature is also to be noted, since it points towards an optimum reaction temperature, say for example, 283K in this case (fig. 1b).

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