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Light polarizer in visible and THz range based on single-wall carbon nanotubes embedded into poly(methyl methacrylate) film

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Abstract
Poly(methyl methacrylate) samples with uniformly dispersed single-wall carbon nanotubes (SWCNTs) were mechanically stretched up to 4 times at 150 °C. As a result, SWCNTs were oriented preferentially along the stretch direction. The width of the angular distribution of the SWCNT orientation determined by polarized Raman scattering and THz absorption spectroscopy was 15 and 12°, respectively. Both methods revealed a high anisotropy of optical response of the composite film. Its application as an efficient polarizer in a wide spectral range from visible to THz is promising.

Keywords: carbon nanotubes, THz spectroscopy, Raman spectroscopy, anisotropy, polymer-matrix composites

(Some figures may appear in colour only in the online journal)

Terahertz (THz) radiation is widely used in different fields like astronomy, spectroscopy, telecommunications, medical and security screening, etc. owing to unique properties inherent to low-energy photons. During the last two decades, efficient emitters, detectors, and other components for THz technologies were developed [1–7]. Among them, high performance polarizers as quasioptical devices for manipulation of THz waves are highly demanded. Several kinds of novel THz polarizers such as liquid crystal polarizers, Brewster’s angle polarizers and wire-grid polarizers [8–14] have been developed basing on different technologies. The structures composed of uniformly spaced metal wires exhibited the high extinction coefficients at THz wavelengths, although they had drawbacks of fragility and structurally tuned architecture not extendable to the broadband THz operation [10].

Carbon nanotubes (CNTs) effectively interact with radiation in the whole frequency range form UV to THz. The isolated SWCNT may be regarded as a 1D object. A small diameter (about 1 nm) and a mean length (few hundreds nm) determine a high aspect ratio of nanotubes. As a consequence, the effects of anisotropic interaction of SWCNTs with the polarized radiation can be observed in processes of light absorption, scattering and so forth. It allows creating anisotropic materials with nanotubes aligned along the preferable direction [15–18], which is quite promising for fabrication of novel optical elements.

Various methods were proposed to form the structures of ordered CNTs. Recently, it was proposed to guide the growth of SWCNTs, using the Y-cut of single-crystal quartz substrates [19] and sapphire [20]. It should be mentioned, however, that
the density of nanotubes is strongly correlated with the density of step edges and, consequently, it is difficult to vary it in a wide spectral range, especially, when the uniform close-packed structures are needed.

The idea to use a self-assembly process of CNTs was realized with spin-assembly technique [21], mechanical shearing [22, 23], DNA-assisted liquid crystal formation on hydrophilic layers [24]. A very narrow angular distribution of the SWCNT orientation was demonstrated by means of Langmuir–Blodgett assembly [25] and self-alignment into micron-wide strips [26]. It has been shown that nanotubes tend to orient themselves in the suspension, aligning parallel to the ‘triple line’ liquid–air–substrate [27, 28].

Stretching of polymer matrix with embedded SWCNTs is a prospective method due to its easy reproduction. The strong anisotropy of optical absorption, fluorescence and Raman scattering has confirmed the preferable orientation of nanotubes along the stretch direction [29–33]. Though this method has a natural limit of nanotube alignment (a finite limit of polymer strain) and no complete alignment or suppression can be achieved, it demonstrated a very good reproducibility and provided an easy mass production.

In this paper, we oriented SWCNTs in poly (methyl metacrylate) (PMMA) matrix by uniaxial stretching of composite. The alignment of SWCNTs was estimated by polarized Raman and THz absorption spectroscopy. The composite film exhibited a high anisotropy of optical properties in a wide spectral range, from THz to visible.

SWCNTs were produced by arc-discharge method, the mean diameter was 1.35 nm [34, 35]. Raw nanotubes were dispersed in chloroform; the bundles of nanotubes were disaggregated by the ultrasonic tip Hielscher UP200 at the power of 200W during 1h. The dispersion of SWCNTs was added to PMMA (10 wt%) solution in chloroform and mixed at a magnetic stirrer during 2h. The weight content of SWCNTs in the final suspension was 0.01%. The suspension was poured into a Petri cup, chloroform was evaporated during 24 h, and after that a free-standing composite film was formed. The film thickness was about 0.5 mm.

To align SWCNTs along a certain direction, the composite film was stretched uniaxially. PMMA is a thermoplastic polymer, which becomes stretchable at temperature above 120 °C. The film, placed between two clamps, was heated by a heat gun up to 150 °C. Then, one of the clamps moved with a constant speed 0.15 mm min⁻¹, and the film was stretched up to four times.

Raman scattering in SWCNTs was excited by radiation of Ar–Kr ion laser (Spectra Physics) with a wavelength of 514.5 nm. The scattered light was registered in the back-scattering geometry. The Raman spectra were recorded using a triple spectrometer Jobin Yvon S3000 with a resolution of 2 cm⁻¹. The film was placed on a rotating plate at the entrance of the spectrometer. The polarized Raman spectra were measured in parallel (VV) and crossed (VH) orientations of the polarization of the incident and scattered light.

The anisotropic electromagnetic response in the THz frequency range was measured by two independent ways: first, by the Fourier spectrometer and, second, with the Novosibirsk free electron laser (NFEL). The transmission spectra were recorded at normal incident angle of linear polarized beam with the parallel and perpendicular orientations of the electric field vector respectively to the stretching direction using a Bruker DFS 66vs vacuum Fourier spectrometer supplied with a pyroelectric detector for the range 30–700 cm⁻¹. The stretched SWCNT/PMMA film was exposed by 1W linear polarized laser beam and rotated around the beam axis.

A typical resonant Raman spectrum of arc-discharge SWCNTs is shown in figure 1(a). In case when the laser excitation wavelength is 514.5 nm, the radial breathing modes (RBM) have a maximum at 180 cm⁻¹ and G-mode has two main components TO and LO, situated at 1592 and 1568 cm⁻¹. The intensity of Raman scattering in unfilled PMMA stretched by the same manner as the composite film is quite low. The weak modes are situated at 260, 370, 490, 605, 1450 cm⁻¹. The Raman spectrum of stretched SWCNT/PMMA film shows the fingerprint modes of SWCNTs. The G-line maximum is slightly shifted to 1590 cm⁻¹ due to the tension caused by the polymer stretch. The modes of PMMA are not distinguishable in the spectrum of composite.

To estimate the alignment of nanotubes in the stretched SWCNT/PMMA film, the Raman spectra were measured for the different relative orientations of the sample and
polarization of the incident light. Figures 1(b) and (c) presents the dependencies of Raman G-mode intensity on the sample orientation. Also the theoretical curves $I_{VV} \sim \cos^2 \alpha$ and $I_{VH} \sim \cos^2 \alpha \sin^2 \alpha$ are shown for comparison. The presence of minima and maxima of the scattered light intensity is an unambiguous sign of nanotube alignment. The experimental data follow well the theoretical curves. However, there is an incomplete suppression of scattering in the minima of the dependencies for experimental data. The simplest explanation of this discrepancy is that there is an imperfect alignment of nanotubes, i.e. instead of one peculiar nanotube orientation there is a certain angular spread and distribution around the direction of the film stretch.

The ratio of Raman intensities at maxima and minima provides the estimation of distribution width of SWCNT orientations. For crossed and parallel polarisations of the incident and scattered light the ratio of intensities in minimum and maximum were 7 and 20, respectively. The Raman signal of the sample is the superposition of scattering from different SWCNTs, oriented in different directions. In VH configuration, for example, this is the following dependence: $I_{VH} = \int \varphi(\theta) \cos^2(\alpha - \theta) \sin^2(\alpha - \theta) d\theta$, where $\alpha$ is the angle between the direction of incident light polarization and the SWCNT axis, and $\varphi(\theta)$ is the angular distribution of SWCNT axis orientations. Assuming the Gaussian shape of $\varphi(\theta)$, the experimental data let us to estimate the width of angular distribution. In case when the film was stretched 4 times, the halfwidth of the angular distribution of SWCNTs was 15°.

The further alignment of SWCNTs was complicated by obvious reasons. First, the stretched polymer/nanotube film after a certain elongation started to crack, and the folds are formed. Second, the alignment of SWCNTs could be hindered, if the nanotubes were crosslinked or bundled.

Due to the high anisotropy of obtained material in the visible spectral range the SWCNT/PMMA composite was investigated in THz region. To exclude the influence of stretched matrix, the transmission spectra polarized along and across the stretching direction for empty stretched PMMA matrix were recorded. The transmission spectra obtained for PMMA are shown in figure 2(a). The absorption bands of polymer are situated at 100, 225, 364, 482, 553 THz. Irrespectively of the orientation of PMMA film, its transmission spectrum is the same. To check additionally the stretching effect, the anisotropy factor $K$ was calculated for the stretched matrix as a ratio of difference and sum of intensities of transmitted light, polarized orthogonal and parallel to the stretching direction: $K = (I_L - \bar{I}_F)/(I_L + \bar{I}_F)$. The coefficient $K$ should be equal to 1 for an ideal polarizer and is zero for an isotropic sample. One can see that for the stretched PMMA matrix the $K$ value is near 0 in the whole investigated frequency range. Hence, it will be no influence of the stretched matrix to the signal registered from the SWCNT/PMMA composite.

Transmission of THz radiation through the stretched SWCNT/PMMA film for two different orientations of the sample to the incident light polarization is presented in figure 2(b). One can see that transmission of THz radiation through the composite depends on the relative orientation of SWCNTs in the sample and the light polarization direction. In case of orthogonal orientation of light polarization and stretching direction the transmission spectrum is quite similar to the spectrum of PMMA matrix with the set of absorption bands specific to the polymer. Otherwise, in case of co-directional light polarization and stretching direction the transmission coefficient is dramatically decreased. The experimental spectrum shows quite a high absorption value for this type of light in the range from 30 to 350 cm$^{-1}$ and a slight increasing in the frequency range higher than 350 cm$^{-1}$.

The anisotropic coefficient $K$ calculated for the investigated composite material is also presented in figure 2(b). As it can be seen the $K$ value lies in the range from 0.4 to 0.97. The maximum $K$ value about 0.97 was registered at 100 cm$^{-1}$. The high value of anisotropic transmission about 0.95 is observed in the frequency range from 50 to 250 cm$^{-1}$. Such a high anisotropy factor indicates that SWCNTs quite effectively absorbed and reflected radiation in case of their orientation in the direction of light polarization. In case of orthogonal orientation of

Figure 2. The transmission THz spectra for orthogonal and parallel orientation of light polarization ($E$) and anisotropy coefficient $K$ for (a) stretched PMMA matrix and (b) SWCNT/PMMA composite. (c) Contribution of nanotubes to transmission spectra of SWCNT/PMMA composite.
the Gaussian distribution of SWCNT orientations, the intensity the distribution width of SWCNT orientations. Assuming to 52. The experimental results provided a possibility to estimate the lowest energy transmitted through the sample is equal m (marked by SWCNT/PMMA film at wavelength of 130 μm (diamonds) in comparison with the experimental results. One can see a good fitting of experimental results by for different widths of distribution. In figure 3 the results can be attributed to the local deviations of nanotubes from the ideal structure. Thus, SWCNT/PMMA composites demonstrated strong anisotropy of optical properties in the wide spectral range from visible to THz.

To summarize, the anisotropic SWCNT/PMMA composites were produced by stretching the polymer films with dispersed filler at elevated temperature. The alignment of SWCNTs was estimated from Raman scattering and THz absorption polarized measurements. The Raman spectra measured in parallel and crossed orientations of polarization of the incident and scattered light showed a strong suppression of the SWCNT G-mode intensity at angles of (2n + 1) × π/2 and n × π/2, respectively. The largest absorption of 130 μm irradiation by the composite was observed when the polarization vector of THz light was parallel to the stretching direction. These results indicated a preferable orientation of SWCNTs in the direction of the applied stretching force. The approximation of angular dependencies of THz transmitted energy and Raman scattering has given a value of SWCNT misorientation of 12 and 15°, respectively. The difference of obtained values of misalignment in the sample for THz and Raman spectroscopy can be attributed to the different sensitivity of these methods to the deviation of nanotube from the straight ideal structure. Thus, SWCNT/PMMA composites demonstrated strong anisotropy of optical properties in the wide spectral range from visible to THz.

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