STUDY ON PROPERTIES OF TiO_2-GO BY TERAHERTZ SPECTROSCOPY

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Abstract

The terahertz time-domain spectroscopy (THz-TDS) is a noncontact tool to measure the optical and electrical parameters of the nanometrics semiconductors/semimetals. Terahertz electromagnetic waves from 0.1 to 10 THz, bounded between the infrared and microwave regions of the spectrum, has been intensively attracted to explore scientific and engineering phenomena for the materials. Terahertz time domain spectroscopy (THz TDS) is a powerful tool for both, to characterize the free carrier response of graphene and probe the inter and intraband response of excited carriers with sub-ps (pico second) time resolution. This work presents application of noncontact THz-TDS techniques and analysis for the terahertz properties of TiO_2-GO in the new generation of optoelectronic devices.

Keywords: Terahertz time domain spectroscopy

Introduction

The far-infrared, or terahertz (THz) region of the electromagnetic spectrum hosts a wealth of intriguing and highly complex interactions between radiation and matter in physical, chemical and biological systems. With photon energies in the millielectronvolt (meV) range, electromagnetic radiation at THz frequencies interacts strongly with systems that have characteristic lifetimes in the picoseconds range and energetic transitions in the meV range. Examples of such systems include bound electrical charges, free charge plasmas, strongly confined charge plasma, excitons, transient molecular dipoles, phonons in crystalline solids, weakly bonded molecular crystals, relaxational dynamics in aqueous liquids, and hydrated biological matter.

Terahertz Spectroscopy is a spectroscopic technique in which the properties of a material are probed with short pulses of terahertz radiation, which consists of electromagnetic waves at frequencies from 0.3 to 3 terahertz (THz). It is proved as a reliable technique for characterization and identification of chemical substances due to characteristic lowest vibrational energy modes of organic molecules. On the other hand, THz radiation can penetrated through most of opaque to visible light materials, for example plastic, paper or cloths. Therefore, pure chemical substances such as explosives and illicit drugs can be detected via THz imaging techniques through the packaging. Moreover, the THz imaging techniques have potential to be used for biomedical microscopy applications and cancer diagnosis (Peter Uhd Jepsen, et.al., (2011)). THz spectroscopy is also found to be an excellent tool for material characterization to investigate optical and mechanical properties. THz spectroscopy was used for qualitative investigation of nanomaterials, polymers, glasses and paper. Oils, both lubricating and edible ones, are also the subject for qualitative and quantitative THz spectroscopy analysis (Ehsan Dadrasnia, (2015)).

For a molecular system, the frequency region for the normal modes spans approximately from tens of to 4000 cm^{-1}. The high frequency normal modes arise from covalent bonds; the upper limit is determined by the stretching modes of O-H and/or N-H bonds, which possess small

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reduced masses. The low frequency normal modes are due to non-covalent interactions, normally featuring intermolecular vibrations and the intra molecular collective vibrations of backbones. The advances in the terahertz (THz) technique in the past two decades have made it possible to generate and detect electromagnetic radiation in the low frequency region, particularly below 100 cm^{-1}, under ordinary laboratory conditions. THz vibrational spectroscopy is therefore a promising tool for molecular characterization.

In this work, we investigate the properties of TiO_2-GO by using terahertz technology.

Terahertz spectroscopy

Recently, it has been demonstrated that THz radiation can be generated using air. Air does not show a second-order nonlinear coefficient, but it has a third order nonlinear coefficient instead. By generating plasma with a pulsed laser, it is possible to mix a fundamental wave and its second harmonic through the third order nonlinearity leading to efficient THz generation. This process opens up the possibility of using THz techniques for remote sensing by propagating a laser beam far from the source, generating THz locally, and transforming the reflected THz radiation into an optical beam again and returning it to the point of origin.

The traditional detection techniques in pulsed THz technology are EO sampling and the use of PC antennas. PC antennas, which are widely used for pulsed THz generation, can also be used to detect THz pulses. Rather than applying a bias voltage to the electrodes of the antenna, a current amplifier and ammeter are used to measure the transient current generated by an optical pulse and biased by the instantaneous THz field. The biased current is proportional to the applied THz field. It is possible to use a PC antenna for broadband THz wave detection by properly selecting the substrate materials. Ultrahigh bandwidth detection has been demonstrated using photoconductive antenna detectors made of LTG-GaAs with detectable frequencies in excess of 60 THz. The apertures of the PC antennas are usually in the micron range, and the optical alignment is more difficult compared to free-space EO sampling.

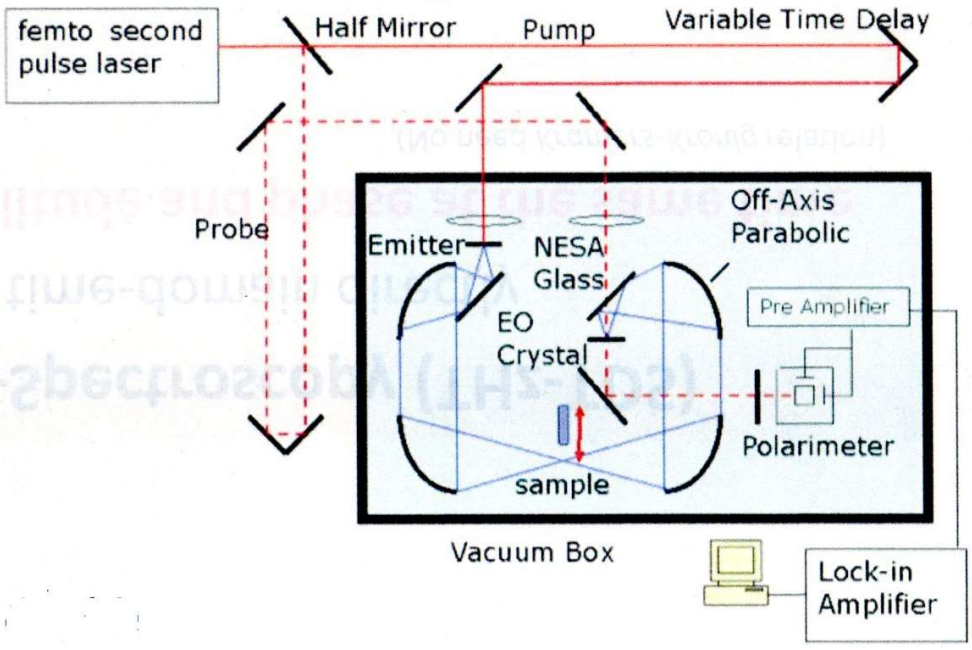

Figure 1 Principle of Terahertz Spectroscopy

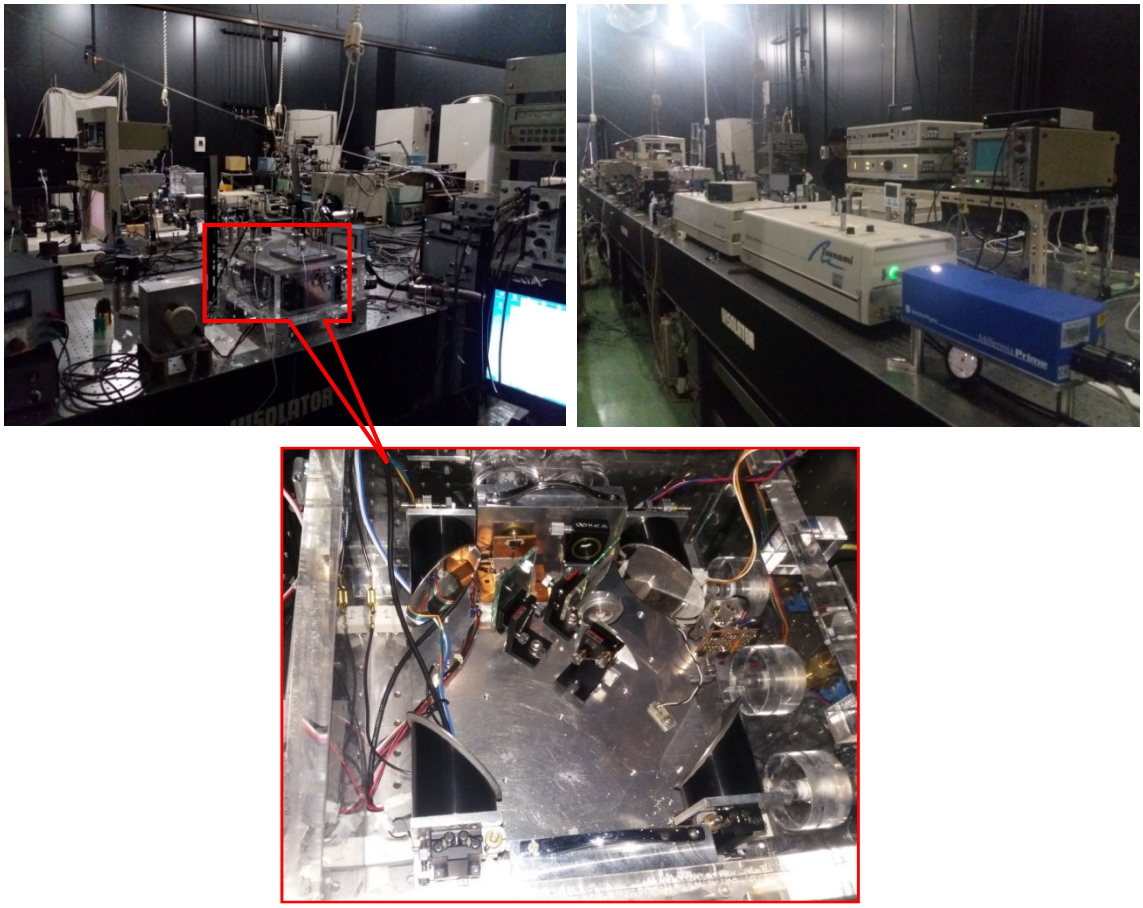

Figure 2 Terahertz Spectroscopy

Material and Method

The anatase TiO_2 powder are collected from commercial and wet milling to form nano crystaline powder. Graphite oxide (GO) make by Hammer's method. 1g of graphite and 0.5g of $NaNO_3$ are mixed with 23ml of H_2SO_4 in ice bath for 30 min. 3g of $KMNO_4$ was added gradually with stirring and cooling the mixture was stirred at 35˚C for 30 min. 46ml of distilled water was slowly added to cause in temperature to 98˚C for 15min. Then, adding 140ml of distilled water followed by 10ml of 30% H_2O_2 solution.

The solid product was separated by centrifugation, washed repeatedly with 5% HCl solution and then washed 3-4 times with distilled water until it turns to ph 6. Finally, graphite oxide gel are obtained by centrifugation.

3.55 ratio of TiO_2/GO are dispersed in DI water with ultra-sonicater and stirring for 3 hours to obtain a homogeneous TiO_2/GO solution. Hydroiodic acid (HI) are added into TiO_2/GO to reduce oxide for 30 mins and then washed 3-4 times with distilled water until it turns to pH 6 and TiO_2/graphene are obtained by centrifugation.

TiO_2/GO solution and TiO_2/graphene are dried in vacuum furnace with different temperature. Then sample and Teflon powder are together made pellet to analysis Terahertz spectroscopy.

Result and Discussion

The absorbance (a.u)Vs frequency (THz) graph of TiO_2 GO/graphene with different annealing temperature sample is shown in Figure 3. It is found that terahertz absorbance of samples are nearly the same under 2 THz frequency for different annealing temperature. But above the frequency 2 THz, it is found that the absorbance is different. It is also found that the absorbance of TiO_2/graphene before dry (black line) is a little shift. It is due to moisture in sample. The between 2 THz and 3 THz band, the transmittance is occur, it is due to intermolecular vibrations does not take place in these regions.

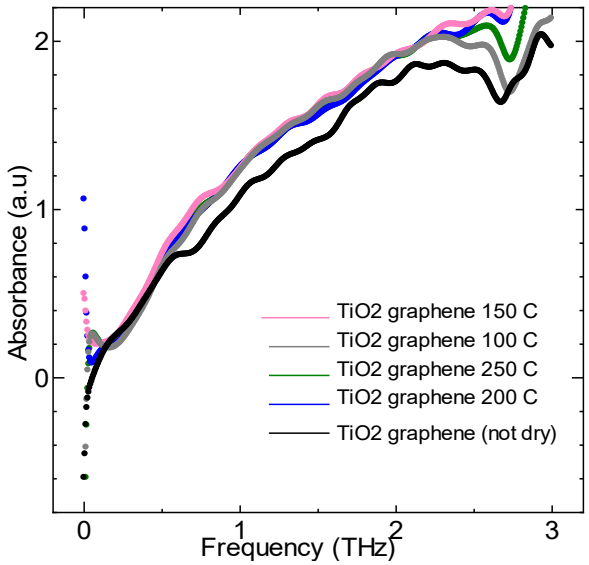

Figure 3 Terahertz absorbance of TiO_2 /graphene at different annealing temperature

Terahertz absorbance comparison of TiO_2-GO and TiO_2-rGO is shown in Figure 4. The absorbance is nearly the same. But the absorbance peak of TiO_2-rGO is occurred in high frequency (2.9 THz). It is due to intermolecular vibrations of graphene. And Figure 5 shows the SEM image of TiO_2-rGO.

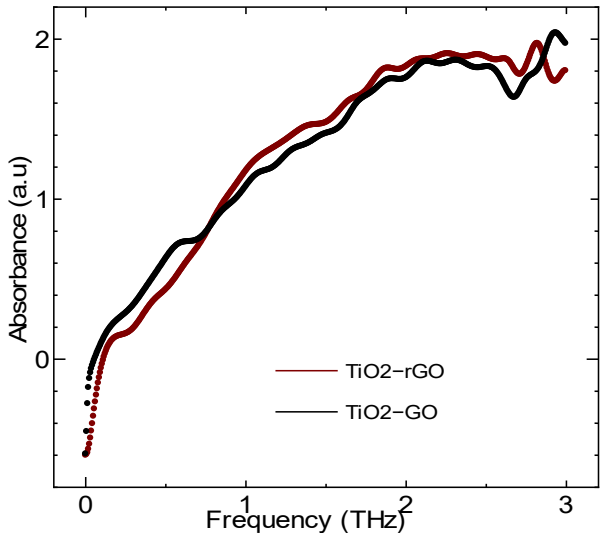

Figure 4 Terahertz absorbance of TiO_2-GO and TiO_2-rGO

Characteristic FT-IR spectra of natural graphite, GO and TiO_2-GO composites (Hui Zhang, Xiaoyan Wang, et. al., (2018)) were shown in Figure 5. All spectra present a broad peak around 3384 cm^{-1} belongs to the bending and stretching modes of O-H groups, and the peak at 1616 cm^{-1} is assigned to the C=O stretching vibration on the GO surface. Also, the peak at 1053 cm^{-1} band is due to the C-O stretching vibrations. These surface oxygen-containing functional groups render the possibility of covalent linkage of TiO_2 onto the GO surface. As for TiO_2-GO composites, the broad absorptions at low frequencies below 1000 cm^{-1} were ascribed to the vibration of Ti-O-Ti and Ti-O-C. This demonstrates that the TiO_2 particle were strong chemically bonded on the GO.

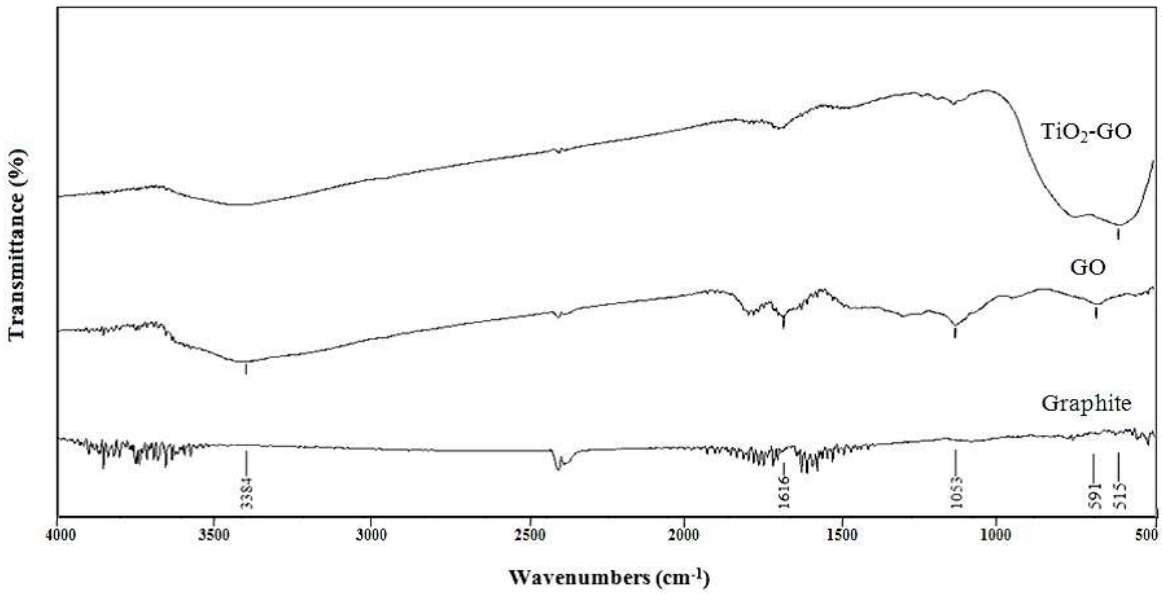

Figure 5 FT-IR spectra of graphite, GO and TiO_2-GO composites.

Figure 6 shows the SEM image of TiO_2/graphene sample. It is found that the graphene layers and TiO_2 are mixed but the sample is not homogeneous.

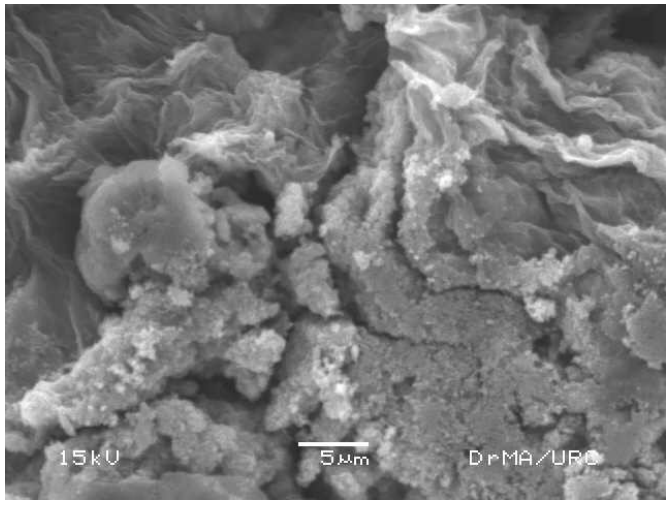

Figure 6 SEM image of TiO_2/graphene sample

Conclusions

This work presents application of noncontact THz-TDS techniques. TiO_2-GO and rGO was studied with different annealing temperature by THz spectroscopic methods. It is not occurred the free carrier response of TiO_2-GO in the THz regions.

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