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Nondestructive Characterization at Nanoscopic Scale by Photoacoustic and Photothermal Techniques -INVITED

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Abstract. Photoacoustic and Photothermal Spectroscopy are excellent techniques for studying the optical absorption spectra of opaque and highly light-scattering substances such as nanomaterials. In this paper we review recent advances in the methodology and its novel applications at the nanoscopic scale.

One of the most challenging problems in nanomaterials research is their accurate characterization, which is fundamental for the efficient use of these technologically promising materials. Absolute absorption, quantum efficiency, thermal diffusivity, and the elastic constants are important parameters for photonic applications. Although the conventional absorption or emission techniques can provide the absorption coefficient, the determination of the absolute absorption is not a trivial measurement due to the presence of scattered light. On the contrary Photoacoustic (PAS) and Photothermal Spectroscopy are very sensitive techniques, immune to scattered or reflected light, and easy to be used to measure the absolute absorption in many different wavelength ranges.

In this summary we review recent advances in the methodology of PAS and its novel applications. In particular we highlight some works done to detect circular dichroism of intrinsic chiral materials [1] as well as extrinsic pseudo-chiral metasurfaces [2], showing how PAS can be applied to measure the selective absorption of circularly polarized light which depends on the orientation of the metasurface. PAS has been also applied to measure the resonant absorption peaks related to the guided modes of GaAs-based NW on Si in the VIS/IR range [3-5].

In disordered media PAS is confirmed to be the most appropriate technique to determine separately the absorption and the scattering coefficients allowing to determine the size of both metallic (AgNP) [6], or semiconductor nanospheres (ZnO) [7,8], or clusters of nanospheres bridged by the ligands [9], in contrast to nanolayered samples [10, 11].

On the other hand photothermal deflection spectroscopy (PDS) may be used as a complementary technique to measure the absorbance spectrum in nanostructures so to detect absorption lines, or photonic band gap in photonic crystals [12], or to evaluate the entity of the scattering phenomena in carbon nanotubes. PDS has been used in the UV/VIS/IR range from 250 to 1200 nm and by using a low modulation frequency from 1Hz to 100Hz which limits the spatial resolution so that the optical and thermal measurements are averaged in the volume.

We also underline some applications of photothermal radiometry (PTR) used to localize the internal heat sources where the pump light is absorbed, and to measure the effective thermal diffusivity. The modulation frequency obtained by an acousto-optical modulator ranges from 1 Hz up to 100 kHz, allowing the improvement of the thermal resolution till submicron range. We have applied PTR to PCM: VO_2 nanolayered samples and SiO_2/VO_2 synthetic opals [13, 14]. The pump beam is partially absorbed in the whole structure. Assuming that the heat is generated proportionally to the light intensity flowing in the structure, one may visualize the internal light propagation by performing the heat depth profile reconstruction from the photothermal radiometric data. This technique has been applied also to carbon nanotube film deposited onto a silicon substrate: in this case PTR allows to detect the thermal wave interference in the film and to measure the effective thermal diffusivity of the CNT, the thermal resistance with the substrate, and the infrared emission property of the CNT [15].

Photothermal radiometry and thermography can be also used to measure the emissivity of nanostructured materials, nanoantennas and metasurfaces which can be designed so to have specific directional thermal emittance properties [16, 17].

But in order to investigate the thermal properties at a nanoscopic scale one should necessarily work at higher frequencies in the MHz range, so to reduce the thermal diffusion length increasing the spatial resolution. One way is definitively offered by laser picosecond acoustics, by using for example a method known as optical heterodyne force microscopy (OHFM) [18, 19]. This detects photothermally induced surface vibrations in an AFM,

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and can image subsurface nanoscale features through their effect on the surface displacement produced by a megahertz thermal field that is optically excited directly below the scanning AFM tip. Alternatively the thermoelastic properties of nanomaterials can be probed through imaging MHz variations in thermoreflectance in combination with picosecond ultrasonics [20, 21].

The invited talk summarizes several research topics and works done in collaboration with the Italian National Research Council, the University of Bath, the University of Dayton, the Tampere University of Technology, ICMM – CSIC in Madrid, the IOFFE Institute in S.Petersburg, and the Hokkaido University in Sapporo.

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