# Optical properties of nano-objects: Carbon nanotubes and metallic particles

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Nanoscience and nanotechnology are in the focus of contemporary research regarding the study of physical and chemical properties of matter in the nanoscopic regime and the exploitation of the gained understanding to revolutionize existing applications or invent new ones. Any such attempts can only be accomplished if methods to "see" nanostructures exist. The optical properties of nano-objects are strongly size-dependent due to confinement effects and consequently technologically interesting for tailoring the optical response of devices. Apart from constituting an interesting field of research on their own, they also provide a unique and non-destructive probe for the identification and study of these structures.

Carbon nanotubes belong to the category of one dimensional nanostructures with typical lengths around 1 μm but very small diameters in the range of 1 nm. The nanotube can be considered as a seamlessly rolled single graphitic layer (graphene) along a folding vector, the chiral vector, which uniquely identifies the tube by the vector's integer components (*n*, *m*) expressed with respect to the graphene lattice vectors [1]. Consequently, the tube properties can be related to the electronic and phononic properties of graphene being modified by the folding of the Brillouin zone. Concerning their electronic properties, the folding scheme can describe two important properties which depend on the "cuts" of the graphene zones due to folding: (a) the nanotube can be metallic if $2n+m$ is a multiple of three or semiconducting elsewise, (b) van Hove singularities appear in the electronic density of states, the optical transitions between which dominate their absorption and their energy scales with the inverse of the tube diameter as expressed in the so-called Kataura plot [2]. More recently, the observation of strong excitonic effects has complicated this picture [3,4,5]. Among optical properties, the Raman effect is extremely interesting and useful in carbon nanotubes [4,5]. Due to its resonant nature, strong Raman signals are available, originating only from the tubes in resonance with the laser excitation. Furthermore, the radial breathing modes (RBMs) of the tubes, being inversely proportional to the tube diameter can be used to distinguish among the different individual nanotubes that are in resonance [6].

Pressure is a particularly useful external parameter for the study of carbon nanotubes [7]. It results in diameter dependent deformations of the tube cross-section, leading to the loss of resonance and disappearance of the RBMs [8,9]. Our studies with carotene encapsulating carbon nanotubes support the pressure induced structural changes by monitoring the Raman signal of the encapsulated molecular species and demonstrate the pressure screening function of the tube [10]. Bundling can alter the evolution of these effects resulting in less hydrostatic pressure transmitting conditions as indicated by Raman measurements of bundled and individual single-walled carbon nanotubes [11]. In double-walled carbon nanotubes the outer tube provides pressure screening for the inner tube and the internal one, structural support for the outer. Pressure application on the inner tubes is realized through their interaction with the outer ones and consequently it is modulated by the inner-outer tube distance and reflected in the RBM and the tangential modes pressure response [12,13]. The resonant nature of the Raman signal from the inner tubes can be used for a rough estimation of their pressure induced band gap changes [13]. This would be impossible by standard absorption measurements since resonances of the inner and outer tubes overlap in wavelengths and the tube-tube interactions broaden and attenuate the experimental peaks. A simple model of anharmonically coupled anharmonic oscillators provides the basic physical picture of pressure application on the RBMs of double-walled nanotubes and can be generalized for multiwall carbon nanotubes [14] allowing the interpretation of the experimental data in these systems [15]. Finally, the understanding of the pressure response of the RBMs can be used to identify the inner and the outer tube pairs in double-walled nanotubes materials [16].

The optical properties of metallic nanoparticles are by far dominated by the well known surface plasmon resonance (SPR), often referred to as localized SPR (LSPR) for the case of nanoparticles, predominantly studied in particle ensembles both in the linear and the non-linear regime [17,18,19]. Noble metals, silver in particular, provide a convenient material for the study of such effects as the interband absorption is well separated by the SPR feature, whereas in gold, it partially overlaps with the SPR and has to be also taken into account. The SPR absorption originates from dielectric confinement of the metal within a dielectric matrix. When the metal fraction is low, the particles are spherical and well-dispersed and the nanoparticle size considerably smaller than the wavelength of the incident light, it is easy to define an effective dielectric function of the composite medium as a combination of the bulk dielectric functions of its constituents. The result is a pronounced and relatively narrow absorption peak, describing a resonant interaction between the electric field and the collective material

excitations (electron density fluctuations). The effective medium approach is equivalent to keeping the dipolar term in a full Mie scattering treatment of the problem, which is inevitable for large particles, whereas for very small particles, size-confinement has to be considered as well. The use of the the pump-probe technique in the study of such effects has been proven fruitful [19]. Size-dependent confinement is evident in electron-electron and electron-phonon interactions, which do not depend on the environment as revealed by measurements in different matrices [20,21]. In order to account for these observations, the "spillout" of electrons outside the particle lattice and the *d* electron wavefunction localization in the inner region of the particle has to be considered in a core-shell model of the particle. The long time response is dominated by coherent acoustic vibration (breathing vibration) of the particles and energy exchanges with their environment. The frequency of the breathing vibration appears unaffected by the environment, unlike its damping which "probes" the local environment and the pressure induced local alterations of the metal-matrix interface [22,23].

Nevertheless, any results on nanoparticle ensembles include non-homogeneous contributions due to the precise size, shape and local environment of each nanoparticle. Ideally, only the study of individual nanoparticles can confidently elucidate the contribution of each parameter to the observed optical properties, and in this context, we have demonstrated the applicability of a far-field optical technique in the study of individual nano-objects [24]. In the concept of Spatial Modulation Spectroscopy, nano-objects are dispersed so that their surface density is smaller than one particle per square micron on a transparent plate that can be scanned in X-Y. A beam is tightly focused on the surface by an objective and collected from the other side by a similar objective. A small amplitude sinusoidal modulation of the particle position leads to the modulation of the optical transmission signal detected by a silicon photodiode, which can be finally demodulated by a lock-in amplifier. By careful measurement of the experimental parameters (e.g. beam diameter), the *absolute* extinction cross-section of the individual particles can be deduced, as it was demonstrated for gold nanoparticles as small as 5 nm in diameter [24]. Furthermore, polarization dependent measurements can reveal shape distortions and the ellipticity of oval particles can be deduced, as well as the local refractive index of the matrix around the particle, which exhibits deviations [25,26]. Of course, any other nanoscopic object, like gold nanorods, can be detected and studied and their spectra can be used to characterize the particles [26]. This method provides a fast locating method of nanoparticles and therefore it can be combined with other optical techniques using the same optical path to study their non-linear optical properties as well [26]. Currently, the method is being applied for the study of individual nanotubes and semiconductor nanorods.


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