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Collective optical resonances in networks of metallic carbon nanotubes

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We demonstrate that thin films of randomly oriented metallic single-walled carbon nanotubes possess optical resonances with significant dispersion. The resonances are observed in the Kretschmann configuration as minima in reflection spectra close to 400 nm and 700 nm wavelengths. The dispersions are visible only when the material is excited with *s*-polarized light, and most prominent in layers with thickness near 100 nm. We conclude that magnetic plasmon polaritons arising from intertube interactions are a likely explanation. Closeness of the M_{11} and M_{22} transition energies to the observed resonances points to a possible coupling with excitons.

Carbon nanotubes (CNTs) have gathered huge interest due to their unique mechanical and electric properties. However, they show great promise also for new optical nanostructures. Due to the van Hove singularities in their density of states, they have distinct optical resonances with excitonic characteristics [1]. In addition, CNTs may also possess plasmonic properties. In electron energy loss spectroscopy π-plasmons have been observed in unsorted single walled (SW) CNTs showing a prominent dispersion between the energies 5 and 10 eV; and $\pi + \sigma$ -plasmons appearing similarly at 15-25 eV [2].

Despite a variety of theoretical predictions (see [3] and references therein), few experimental results exist on optical plasmons in CNT materials. Surface plasmon polaritons (SPPs) excited by a commonly used total internal reflection (TIR) setup, the Kretschmann configuration (see Fig. 1a), have been shown to couple through an array of vertical multi-walled CNTs [4]. In addition, composite materials of SWCNTs can show localized surface plasmon resonances (LSPRs) dependent on tube length [5].

In this article we demonstrate dispersive and polarization dependent optical modes excited via the Kretschmann configuration within a randomly oriented planar network of metallic SWCNTs.

The used SWCNT materials were purchased from NanoIntegris Inc. (Menlo Park, CA, USA), and consisted of arc discharge produced SWCNTs with a mean diameter of 1.4 nm. The SWCNTs had been enriched to either high metallic or semiconducting concentrations (98 %) using density gradient ultracentrifugation. The material was deposited on glass slides as described in the Supplementary material. The formed layers consist of randomly oriented CNT networks consisting mainly of bundles, as seen in Fig. 1b and c.

Reflection spectroscopy was performed on the SWCNT networks, using the Kretschmann configuration with a varying excitation angle and a collimated white light source, as shown in Fig. 1a and Supplementary material. The measurements with *s*-polarized light showed a

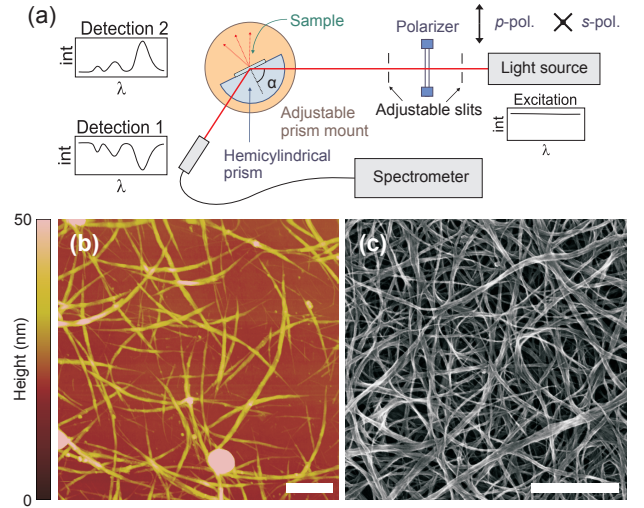*Corresponding author. E-mail address: j.jussi.toppari@jyu.fi

FIG. 1: (a) Schematics of the measurement setup utilizing Kretschmann configuration. (b) Atomic force microscope (AFM) image of a typical thin network of metallic SWCNTs. (c) Scanning electron micrograph of a thick network of metallic SWCNTs. All the scale bars are 500 nm.

clear dip moving from 600 to 800 nm as the excitation angle, α, relative to the sample normal increased (see Figs. 2 and 3a). A similar feature was also found around 400 nm. With *p*-polarized excitation no clear dispersion was observed, and only a spectrum similar to the transmission of the sample was visible as shown in Fig. 3a. Control samples prepared similarly but using semiconducting (Fig. 3d) and unsorted (Supplementary material) SWCNTs did not display any dispersive features.

To test the influence of the surrounding medium on the resonances, the metallic SWCNT layers were measured within additional media. When embedding the SWCNT film in isopropanol ($n_{air} = 1.00 \rightarrow n_{IPA} = 1.38$), the dispersive resonances appeared at the same energies, but with shifted and more prominent angle dependence, as shown in Figs. 3b and 2b. Changing the surrounding medium to water yielded similar response (see Supplementary material). Instead, evaporation of 50 nm of gold on top of the SWCNT film destroyed any previous dispersive resonances: only the stagnant transmission spectrum
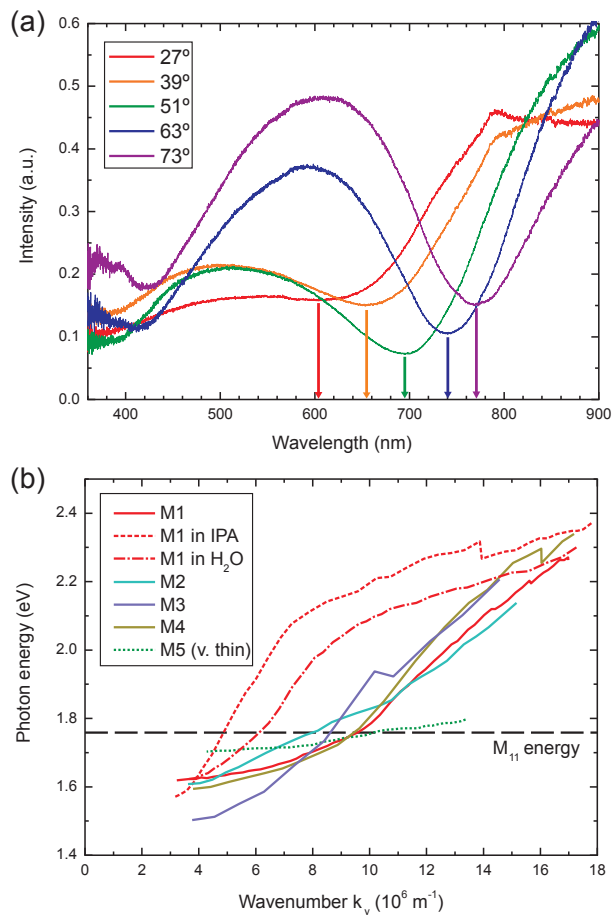
FIG. 2: (a) Reflection spectra from a metallic SWCNT network (sample M2). Excitation angles are given relative to the sample normal. (b) Dispersion curves, i.e., minimum of the dip in the reflectance spectrum as a function of a vertical component of the wavevector, k_y, measured from various metallic SWCNT film samples. M1 is measured in air, as well as embedded in isopropanol and water; others only in air. Samples M1-M4 are roughly 100 nm thick, while M5 is only 5 nm thick.

FIG. 3: Intensity of reflected light as a function of the excitation angle and the wavelength for $\sim$100 nm thick SWCNT networks. (a) Sample M1, which has metallic SWCNTs. The observed resonances are visible with s-polarization at angles above the TIR angle, $\sim 41°$. (b) M1 embedded in isopropanol. The resonances appear again with s-polarization at angles above the TIR angle, $\sim 65°$. (c) Sample M4 with metallic SWCNTs and a 50 nm Au coating on top. Typical SPP resonance is visible at p-polarization. (d) Sample with semiconducting SWCNTs. Transmission spectrum for each sample is also visible on the right, except for (b), where transmission was measured without isopropanol.

of the SWCNTs was visible at s-polarization, and the characteristic surface plasmon resonance of a gold layer is seen with p-polarized excitation, as shown in Fig. 3c. The described resonances have also a clear dependence on the thickness of the SWCNT layer, being more pronounced near 100 nm thickness, see Fig. 4. Very thin ($\leq$ 20 nm) and thick (≥ 0.5 μm) layers do not have the dispersive resonances in their reflectivity spectra as shown in Fig. 2b, where the observed dispersions of different samples and environments are collected.

In our case the resonances are observed at s-polarization, where the electric field of the optical excitation is parallel to the rotation axis of the Kretschmann configuration, and changing the angle does not affect its projection. On the other hand, the magnetic field of an s-polarized photon is perpendicular to the CNT film, and thus the angle makes a difference in terms of momentum,
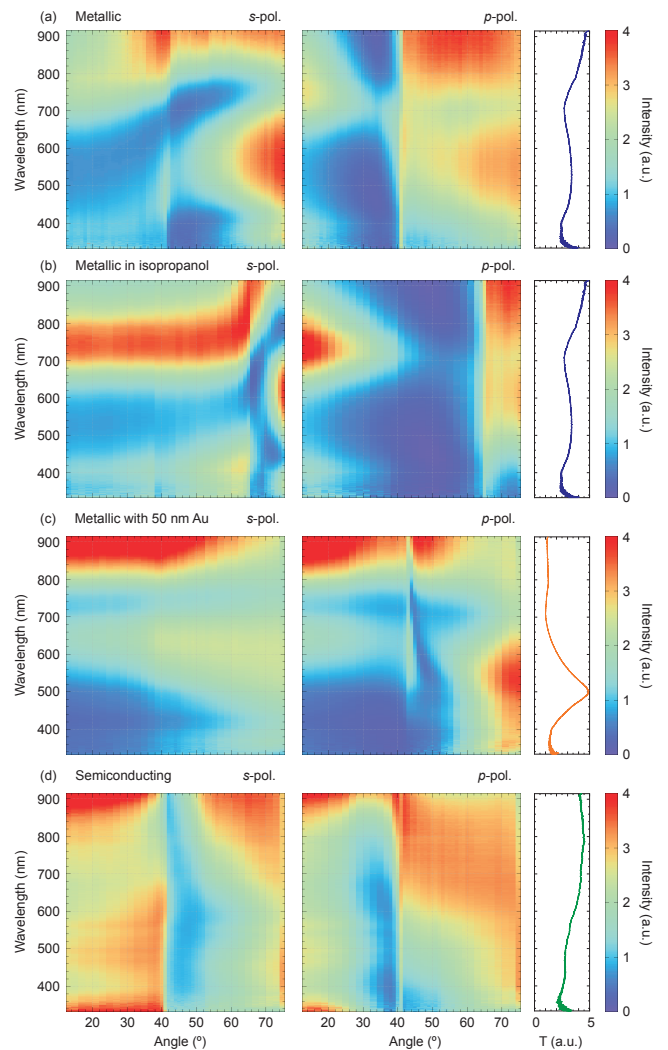
and could imply a dispersive behavior. One possible interpretation agreeing with the observed phenomenon is thus magnetic resonances within the network [6], excited by the magnetic field of the excitation light.

The thickness dependence of the resonances further points to a collective resonance similar to electric SPPs, which can only be excited with p-polarized light in thin metal films. If the metal is too thin in the case of SPPs excited via the Kretschmann configuration, the SPP will be weak because of radiation damping into the glass. As
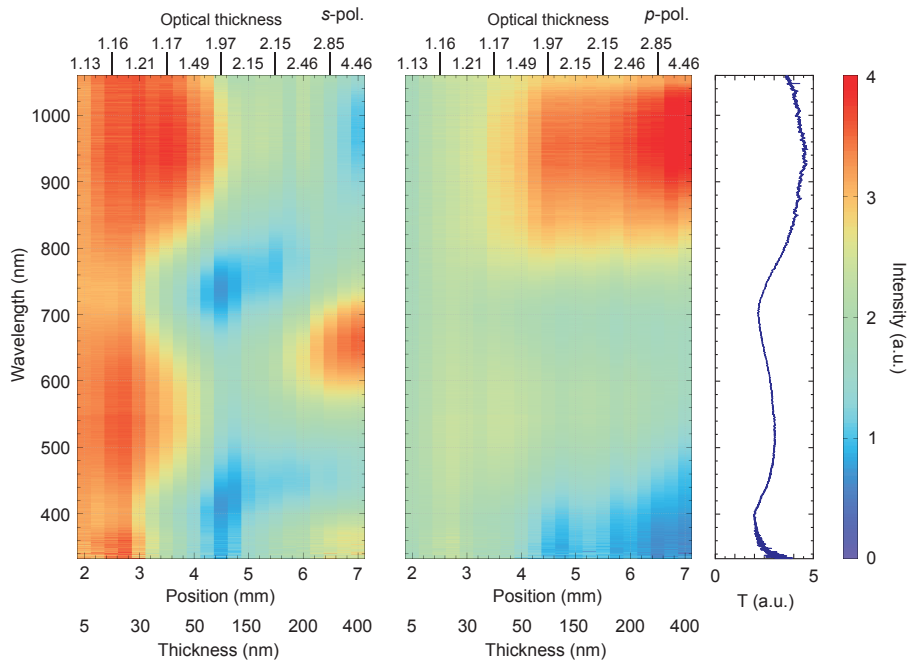
FIG. 4: Intensity of the reflected light as a function of the network thickness and wavelength for metallic SWCNTs. Excitation angle is 51°. Optical thickness refers to transmission intensity at 900 nm wavelength divided by the intensity at 700 nm (close to the M_{11} resonance). Position refers to location on the glass sample parallel to the plane of incidence and the thickness is measured with AFM. The transmission spectrum at right is taken at the position 4.5 mm.

for a thick film, the SPP cannot be efficiently excited due to absorption in the metal. Similar mechanics with magnetic fields could produce the same dependence in a SWCNT film if the excitations appear at the surface [7]. These resonances could be for example magnetic plasmon resonances (MPR) formed due to coupling and regular spacing of SWCNTs within bundles. In this case the bundle acts like a lattice of nanowires with uneven endpoints [6]. Further, these resonances could enable a collective magnetization wave to propagate at the surface of the film. These magnetic plasmon polaritons (MPPs) are a likely explanation because s-polarized MPPs have strong dispersion whereas p-polarized ones are non-dispersive [8]. This interpretation is further supported, in addition to the thickness dependence, by the sensitivity to the dielectric environment, and it would also hint at a negative magnetic permeability in the material [7]. The effective dispersion also changes, because for very thin films at the M_{11} and M_{22} transition energies only normal absorption will be visible, which has no angle dependence.

Gap plasmon modes could also explain the observed phenomenon. However, these modes should depend on the length of the gap, i.e., in this case the length of the SWCNTs in bundles. To test this, a new sample was fabricated out of CNTs shortened by an extensive sonication. This resulted in a similar bundled film, but the resonances were still at the same energies; only weakened in intensity, most probably due to the additional amorphous carbon. Furthermore, LSPR in catalyst metal nanoparticles left over from the CNT synthesis would not dis-

play dispersion, and any possible combination with CNTs would have resonances dependent on the tube length. Thus, this possibility can also be ruled out.

Notable is that the dispersive resonances around 600-800 nm and 400 nm are close to the M_{11} and M_{22} transition energies of metallic SWCNTs, respectively (Figs. 2b and 3a). This raises the question whether exciton creation is causing the optical resonances. Excitons can have momentum dependence in periodic systems, but in the measured SWCNT films also the thickness affects the intensity of the resonance, which is not fully consistent with an excitonic resonance. However, an exciton–plasmon state could be responsible for the resonances in our system [9]. Graphene sandwiched between glass and polymer has also shown to pose an excess broadband absorption at s-polarization in TIR [10]. However, further experimental and theoretical studies are needed to confirm the underlying mechanism of the observed dispersive optical resonance.

In conclusion, we have observed a clearly dispersive optical resonance in reflection spectroscopy of metallic SWCNT films. It appears only for an s-polarized excitation source, and is strongest at film thicknesses around 100 nm. The dependence of intensity and dispersion of the resonance on the thickness and the surrounding environment is consistent with creation of magnetic plasmons or MPPs, and the vicinity of M_{11} and M_{22} transitions suggests that excitons may be involved in the process.

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