THz response of TiO₂ microspheres embedded in a dielectric layer

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Abstract—TiO₂ microspheres embedded in a dielectric layer were investigated both experimentally using time domain terahertz (THz) spectroscopy, and theoretically by finite-difference time-domain method. We focus on the role of the permittivity of the embedding medium. We find that media with sufficiently low permittivities do not significantly affect the effective response of the microspheres, which is a prerequisite for the fabrication of durable metamaterials with fixed spatial distribution of the components.

I. INTRODUCTION

Metamaterials are artificial electromagnetic media structured on a sub-wavelength scale with unique effective optical properties. TiO_2 microspheres represent a Mie resonancebased dielectric metamaterial [1]. The effective response relies on the resonance of individual elements. This is in contrast with photonic crystals where the properties stem namely from their periodicity [2]. In the previous study [3], a monolayer of microparticles randomly distributed in air was investigated. Here, TiO_2 microspheres were embedded inside a low loss dielectric environment and a magnetic activity in the terahertz range was demonstrated.

II. RESULTS

We developed a bottom up approach allowing fabrication of tens-micron diameter dielectric resonators. First, a liquid suspension of TiO₂ nanoparticles was sprayed through a flame. This results in fragile TiO₂ microspheres which were subsequently sintered in a furnace at high temperatures (1200 -1400°C) for hours, in order to consolidate individually each sphere and minimize its porosity [4], see Fig. 1. The microspheres were finally sieved and sorted along their diameters in order to obtain microspheres with various diameters and with narrow size distribution.

The microspheres were mixed with powder polyethylene ($\varepsilon = 1.99$) and 14 MPa pressure was used to prepare thin (< 1 mm) pellets with random distribution of microspheres. We observed that higher pressure (28 MPa) can damage TiO₂ microspheres, thus effectively killing the resonance.

Transmission and reflection spectra along with the effective parameters were calculated using MEEP package [5]; their examples are shown in Fig. 2. The homogenization of our structure is based on the extraction of effective material parameters from reflection \tilde{r} and transmission \tilde{t} coefficients for normal incidence of the plane wave [2], [6].



Fig. 1. Scanning-electron-microscope image of TiO_2 microparticles. Quality of the microspheres is demonstrated in the insets.

The lowest-order Mie resonance is located at 0.8 THz and its position changes only weakly for $\varepsilon < 3$. However, the strength of the negative effective permeability decreases with decreasing contrast between ε of resonators and embedding medium. The range of the negative μ_{eff} completely disappears for embedding material permittivity > 3. The Mie resonance is responsible for the strong absorption at resonant frequency: the transmission is around 20 % for a single layer of TiO₂ with filling factor 12.8 % in the air and it further decreases with increasing permitivity of the host material.

The samples were characterized using a TeraView TPS Spectra 3000 THz spectrometer. Transmission through an empty aperture, 1.02 mm thick polyethylene pellet and 0.91 mm thick polyethylene pellet with low concentration (0.7 volume percents) of TiO₂ microspheres with diameters in the range $38 - 40 \,\mu\text{m}$ was measured (Fig. 3). The transmission spectrum of PE pellet is modulated by internal reflections inside it. There is only a very low absorption which demonstrates very good dielectric properties of polyethylene as the host material. In the pellets containing the TiO₂ microspheres, we can observe response similar to the pure PE pellet at low frequencies. Around 0.8 THz a sharp decrease in transmission appears due to the lowest Mie resonance in the TiO2 microspheres. This suggest a good quality of the TiO₂ microsphere ensemble - particles are spherical and their size distribution is narrow. The absorption sharply increases with the increasing concentration of TiO₂ microspheres.



Fig. 2. Calculated effective permeability (left panel) and transmission |t| (right panel) of TiO₂ microspheres embedded in a medium with variable permittivity. Parameters of calculations: single layer of TiO₂ microspheres with a diameter of 40 μ m was arranged in a square lattice with the volume of elementary cell $64 \times 64 \times 64 \mu m^3$.

For more quantitative measurements each sample was placed between two thick sapphires. This arrangement made it possible to simultaneously determine the transmission and the reflection spectrum, which can be used for the determination of their effective permittivity and permeability [3]. The presented waveform (Fig. 4) qualitatively differs from the previous measurement [3] as the internal reflections do not completely overlap in time and they can be resolved in time. Preliminary results suggest that Gouy shift [7] can not be neglected in the analysis of these thicker samples. We are now working on the precise extraction of the effective permeability and permittivity.



Fig. 3. The spectral response of the empty aperture, the pure polyethylene pellet and the polyethylene pellets with low concentration of TiO_2 spheres is plotted.

III. CONCLUSION

Resonant frequency of TiO_2 microparticles is controlled by their permittivity and dimensions, whereas it is almost



Fig. 4. Transmission measurement of THz pulse through sapphire polyethylene pellet with low concentration (0.7 % of TiO₂ microspheres with diameters in the range $38 - 40 \,\mu\text{m}$ - sapphire. In the inset, the scheme of our experiment is given [3].

independent on the filling fraction and on the permittivity of the surrounding dielectric medium ε . Strong resonance can be observed even for a low filling factor.

Polyethylene was found to be suitable medium for accommodating TiO_2 microspheres and preserving their Mie resonance. Transmission spectrum of PE pellets with a low concentration of TiO_2 was experimentally observed and the absorption sharply increases with the increasing concentration of TiO_2 microspheres.

IV. ACKNOWLEDGEMENTS

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REFERENCES

- Q. Zhao, J. Zhou, F. Zhang, and D. Lippens, "Mie resonance-based dielectric metamaterials", Materials Today, vol. 12, pp. 60-69, 2009.
- [2] F. Dominec, C. Kadlec, H. Němec, P. Kužel, and F. Kadlec, "Transition between metamaterial and photonic-crystal behavior in arrays of dielectric rods", Optics express, vol. 22, pp. 30492-30503, 2014.
- [3] H. Němec, C. Kadlec, F. Kadlec, P. Kužel, R. Yahiaoui, U. C. Chung, et al., "Resonant magnetic response of TiO2 microspheres at terahertz frequencies", Applied Physics Letters, vol. 100, pp. 061117, 2012.
- [4] O. Mitrofanov, F. Dominec, P. Kužel, J. L. Reno, I. Brener, U. Chung, et al., "Near-field probing of Mie resonances in single TiO2 microspheres at terahertz frequencies", Optics express, vol. 22, pp. 23034-23042, 2014.
- [5] A. F. Oskooi, D. Roundy, M. Ibanescu, P. Bermel, J. D. Joannopoulos, and S. G. Johnson, "MEEP: A flexible free-software package for electromagnetic simulations by the FDTD method", Computer Physics Communications, vol. 181, pp. 687-702, 2010.
- [6] D. R. Smith, S. Schultz, P. Markoš, and C. M. Soukoulis, "Determination of effective permittivity and permeability of metamaterials from reflection and transmission coefficients", Phys. Rev. B, vol. 65, pp. 195104, 2002.
- [7] P. Kužel, H. Němec, F. Kadlec, and C. Kadlec, "Gouy shift correction for highly accurate refractive index retrieval in time-domain terahertz spectroscopy", Opt. Exp., vol. 18, pp. 15338-15348, 2010.