Abstract Monocrystalline titanium dioxide (TiO\textsubscript{2}) micro-spheres support two orthogonal magnetic dipole modes at terahertz (THz) frequencies due to strong dielectric anisotropy. For the first time, we experimentally detected the splitting of the first Mie mode in spheres of radii 10 – 20 \(\mu\)m through near-field time-domain THz spectroscopy. By fitting the Fano lineshape model to the experimentally obtained spectra of electric field detected by the sub-wavelength aperture probe, we found that the magnetic dipole resonances in TiO\textsubscript{2} spheres have narrow linewidths of only tens of gigahertz. Anisotropic TiO\textsubscript{2} micro-resonators can be used to enhance the interplay of magnetic and electric dipole resonances in emerging THz all-dielectric metamaterial technology.

Splitting of magnetic dipole modes in anisotropic TiO\textsubscript{2} micro-spheres.

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1. Introduction

Sub-wavelength dielectric resonators are the building blocks of all-dielectric metamaterials [1–5] and metasurfaces [6–8] - artificially created materials with engineerable effective dielectric permittivity and magnetic permeability or local impedance. The required macroscopic magnetic response [9] in such non-magnetic structures is realised through arranging sub-wavelength dielectric resonators, sustaining magnetic dipole modes [10], in an array.

Spectrally overlapping magnetic and electric dipole modes in a dielectric resonator create a Huygens source [11], which can be a base for reflectionless all-dielectric metasurfaces. To achieve such overlapping, either substrate effects [12, 13] or geometrical anisotropy [7, 8] can be employed. Material anisotropy, such as in mono-crystalline TiO\textsubscript{2}, in geometrically-isotropic dielectric resonators can lead to similar effects. Moreover, anisotropic dielectric resonators give an additional degree of freedom for collective resonant effects [14].

To form a metamaterial, resonant 'meta-atoms' have to be packed at a scale significantly below \(\lambda/2\), where \(\lambda\) is the resonance wavelength in free space. To sustain electromagnetic resonances at a sub-wavelength scale sufficient for the effective medium approximation in all-dielectric metamaterials, constituent resonators have to be made of materials with high values of dielectric permittivity.

At optical frequencies, it is hard to find such materials and, thus, to achieve strong resonant confinement: silicon resonators with dielectric permittivity of \(\varepsilon = 16\) resonating at a wavelength of \(\lambda = 800\)nm are only \(\approx \lambda/4\) in size [15], where \(\lambda\) is the resonance wavelength in free space. This makes it barely possible to pack such resonators at a sub-wavelength scale (with pitch significantly below \(\lambda/2\)) to form a metamaterial or a metasurface. In the terahertz (THz) frequency range, high values of dielectric permittivity are not unusual. TiO\textsubscript{2} micro-spheres with \(\varepsilon \approx 100\) confine electromagnetic energy resonantly within a space with linear dimensions on the order of \(\lambda/10\) [16, 17]. Allowing for sub-wavelength packing, they are a promising foundation for emerging all-dielectric terahertz metamaterials [18, 19].

TiO\textsubscript{2} can be highly anisotropic [20]: the reported ordinary and extraordinary permittivities of bulk rutile TiO\textsubscript{2} in the THz frequency range are \(\varepsilon_0 \approx 80\) to \(\varepsilon_r \approx 150\). Thus, the orientation of mono-crystalline TiO\textsubscript{2} micro-spheres critically affects their spectroscopic properties. In addition, TiO\textsubscript{2} micro-spheres may show significant variability in morphology, crystallinity, density, shape and surface roughness. So far, the THz spectral signatures of anisotropic TiO\textsubscript{2} micro-spheres have not be measured.
In this paper, we propose and demonstrate a technique for characterising sub-wavelength mono-crystalline TiO$_2$ micro-spheres using near-field THz microscopy [17,21,22]. For the first time, we experimentally detected the splitting of the lowest resonant Mie mode into two distinct magnetic-dipole eigenmodes due to the pronounced dielectric anisotropy of the micro-sphere material. We demonstrate that the intrinsic properties of high-permittivity anisotropic resonators can be extracted despite the undetermined orientation of the crystallographic axes of the constituent anisotropic material. We found that the linewidths of the observed THz resonances are of the order of tens of gigahertz. They also vary significantly among individual micro-spheres measured, indicating that the fabrication process has a critical effect on the resonators’ properties.

**2. Methods**

TiO$_2$ spherical particles, 10 – 40 µm in diameter, are fabricated by spraying TiO$_2$ nano-crystal suspension into a flame and subsequent annealing at 1400 °C. The annealing process melts poly-crystalline particle clusters into mono-crystal TiO$_2$ spheres. X-ray diffraction (XRD) analysis confirmed that the main constituent is TiO$_2$ in the rutile tetragonal phase. It also identified monoclinic Ti$_3$O$_5$ as a minority phase. A scanning electron microscopy (SEM) image of one of the studied samples is shown in the title Figure. SEM analysis showed small voids and inclusions within cracked spheres and also revealed that some micro-spheres contain several large mono-crystal domains.

To investigate Mie resonances, single spheres were attached to a 12.5 µm-thick polyethylene substrates and positioned within several micrometers from a THz near-field probe comprised of a 10 µm × 10 µm aperture in a gold screen and a photoconductive antenna detector behind the screen [21]. The samples were illuminated at normal incidence to the screen plane by a linearly-polarized (z-axis) single-cycle THz pulses generated using a ZnTe crystal. The photoconductive THz antenna detected the $E_z$ component of THz field coupled through the aperture. The near-field response for each sphere was obtained for different angles of rotation in the xy-plane within the spectral range of 0.5 – 2.5 THz.

Full-wave numerical versions of the experiments were performed using the time-domain solver of the CST Microwave Studio®. We modelled the response of anisotropic spheres in the range of 0 – 2.5 THz taking the substrate and the near-field probe into account as in [22]. We set the finite size of the gold screen as 500 µm, which is more than 10 times the diameter of any of the measured samples. We used hexahedral mesh cells with linear sizes varying from 0.3 to 10 µm.

**3. Results and Discussion**

**3.1. Mie resonances**

Two non-degenerate magnetic dipole modes are expected to be excited in a mono-crystalline TiO$_2$ sphere when its optical axis (c crystallographic axis) is not aligned with or not strictly perpendicular to the incident THz field vector (see title Figure). In other words, when the incident electric field has both components parallel and perpendicular to the optical axis of TiO$_2$, it excites two orthogonal magnetic modes: one at a higher frequency (ordinary mode; electric field polarisation plane inside the sphere is perpendicular to the optical axis of TiO$_2$) and one at a lower frequency (extra-ordinary mode; the electric field polarisation plane contains the optical axis of TiO$_2$), see title Figure.

Figure 1 shows typical waveforms of the detected THz field coupled through the aperture of the probe. The incident THz pulse sampled by the sub-wavelength aperture probe is shown in Figure 1(a). Measuring the time-domain response of the micro-spheres, we observed two types of resonant waveforms: Fig.1(b) shows harmonic oscillation of the field that lasts over 20 ps; Fig.1(c) presents an amplitude-modulated oscillation of the field. The first case corresponds to the resonant response of a sample due to the excitation of a single magnetic dipole mode. In the second case, the “beating” indicates the excitation of two resonances simultaneously. The splitting of the modes is discussed in detail in Section 3.4.

The field oscillations in the waveform in Fig.1(b) represent the enhancement of the electric field within a narrow frequency range. The Fourier transform of the waveform Fig.1(b), measured for the sample with radius $r = 10.7$ µm (sample # 1) and normalized to the corresponding reference...
We attribute this to the reduced sensitivity of the experimental system at higher frequencies. 

Figure 2 (a): Experimentally obtained (red curve and squares) and numerically simulated (blue dashed curve) enhanced electric field spectrum of an anisotropic TiO$_2$ sphere of radius $r = 10.7\mu m$ (measured using SEM: inset image) with its main axis oriented perpendicularly to the incident THz pulse polarization plane. The black curve is a Fano model fit with linewidth $\Gamma_o = 76$GHz and resonance frequency $f_o = 1.69$THz: (b) and (c): Schematic spatial distributions of magnetic (blue) and electric (red) fields excited in magnetic dipole modes supported by TiO$_2$ spheres at frequencies below (b) and above (c) the resonance frequency. The insets show the corresponding numerically calculated maps of the $x$-component of the electric field. At each frequency, the sphere is excited by a corresponding standing wave formed due to reflections from the metallic detector. The samples are located between the ground plane of the detector and the first node of the magnetic field, $H_b$. The field leaking through the aperture (and detected by the THz photoconductive antenna in case of $E_r$) is a superposition of the fields induced in the resonator and the background field corresponding to the incident THz beam. 

At frequencies above the resonance frequency, the electric field of the magnetic dipole mode (Fig. 2(b)) interferes destructively with the standing wave (between the ground plane and the first node of the magnetic field $H_b$) in a narrow frequency range. In the measured spectra, we observed characteristic amplitude dips at frequencies slightly below the resonance frequencies of the magnetic dipole modes (highlighted in blue in Fig. 2(a)). 

At frequencies below the resonance frequency, the resonant mode field lags the excitation field, leading to the constructive interference of the modal fields with the standing wave (Fig. 2(c)). Corresponding field enhancement peaks were observed in all the measured spectra (highlighted in red in Fig. 2(a)).
The Fano lineshape of the resonance modes is closely connected to the detection process itself. Our simulations indicate that the Fano lineshape of the detected enhanced near-field progressively changes as the distance between the sphere and the metallic THz probe increases (see insets in Fig. 3(b)).

In the presence of the metallic plate, the polarity of the observed Fano shape depends on the symmetry of the studied mode and the place where it is measured. In case of the magnetic dipole mode discussed here, the ‘polarity’ is reversed at the front surface of the sphere (further edge with respect to the probe), where the resonant electric field has an opposite phase. Therefore, a reversed spectrum - constructive interference below the resonance and destructive interference above the resonance - is expected to be observed at this position. Note that a different near-field detection scheme, including e.g. a scattering-type near-field probe, would be required for such an experiment.

At each frequency, the phase relation between the incident field (standing waves) and the magnetic resonance mode is defined by the position of the sphere with respect to the nodes of the standing wave.

In our experiment, the studied spheres were always placed at distances of several micrometres from the probe: thus, they were always between the ground plane and the first node of the $H_z$ component of the incident magnetic field at the resonance frequency (always below $\lambda_{\text{max}}/2 = 60\mu$m).

### 3.3. Intrinsic properties of dielectric micro-resonators

The intrinsic characteristics of Mie modes, i.e. resonance frequencies and linewidths, are defined by the geometrical and material properties of the resonator. The corresponding experimental values may be also influenced by the presence of the substrate and the metallic probe (ground-plane effect). The aim of this Section is to characterize these dependences.

Unlike metallic micro-objects [22] or dielectric resonators made of low-permittivity materials [26], the resonance modes of the studied micro-spheres are confined within the resonators due to the high dielectric permittivity of TiO$_2$. Therefore, the influence of the low-permittivity substrate (polyethylene) on the observed resonance properties is minimal [27].

To address the effect of the metallic probe on the resonant properties of the samples, we numerically simulated spheres suspended in free space, and spheres placed on top of a perfect electric conductor, which emulated the conditions of our experiment. The resonance frequencies in both cases were found using the far-field scattering cross-section spectra. Figure 3(a) shows the resonant frequencies calculated numerically for identical TiO$_2$ spheres suspended in free space (blue solid curve) and placed on top of a metallic plane (blue dashed curve). The blue squares represent the resonance frequency obtained from fitting a Fano-resonance curve (Eq. 1) to the data obtained via numerical near-field experiment described in Sec. 2. The differences between the three resonance frequencies for all considered radii of the micro-spheres are negligible. The resonance frequency detected in the experiment, therefore, can be considered as the intrinsic frequency of the TiO$_2$ sphere despite the presence of the ground plane of the probe.

In contrast to the resonance frequency, the linewidth of the sphere placed on top of a metallic plane (red dashed line in Fig. 3(a)), is noticeably broadened, by 10 – 15 GHz, as compared to the suspended case (red solid line). The linewidths extracted through Fano-fitting of the data obtained in our near-field numerical experiments (red squares) were confirmed to have values similar to those obtained in
far-field simulations for a sphere sitting on top of and at a 5 \( \mu m \) distance away from a metallic plane.

For a sphere placed within \( \approx 10 \mu m \) from the metallic plane, the linewidth of the Mie resonance of the sphere, extracted through Fano-fitting of its numerical near-field spectra, varies by less than 2 GHz, which is demonstrated in the inset in Fig. 3(a) (red circles). At distances larger than \( d \approx 10 \mu m \), the proposed Fano-fitting method becomes less reliable due to the drop in the resonant field enhancement at larger sample-to-probe distances (inset in Fig. 3(a), black squares). Thus, we conclude that the linewidth extracted by fitting the Fano curve to the measured near-field spectra, can be considered independent of the sample-to-probe distance for \( d < 10 \mu m \).

In contrast, the amplitude \( q \) of the Fano resonance changes significantly even at small sample-to-probe distance (Fig. 3(b)). This is due to the strong near-field confinement of the resonant modes and the interaction of the resonant near-field with the standing waves formed behind the ground plane of the detector (see Sec. 3.2)). We note that the ratio of the resonance frequency to the resonance linewidth, or the quality factor of the resonator, is independent of sphere size. We can conclude that while the Fano lineshape (determined essentially by the amplitude \( q \)) depends strongly on experimental conditions, the measured resonance frequency (and to a large extent also the linewidth for \( d < 10 \mu m \)) do correspond to intrinsic parameters of the observed Mie resonances.

### 3.4. Splitting of magnetic resonance modes due to anisotropy in mono-crystalline TiO\(_2\)

Studying different orientations of the samples in the \( xy \)-plane, we observed two types of spectral signatures: the excitation of a single (either the ordinary or the extraordinary) magnetic dipole resonance or of two resonances simultaneously. The ordinary magnetic dipole modes in TiO\(_2\) spheres have higher frequency than the extraordinary magnetic dipole modes: the electric field of the ordinary magnetic dipole mode lies in the plane where spheres' effective permittivity is \( \varepsilon_o \), which is lower compared to the averaged effective permittivity of \( \varepsilon = (\varepsilon_o + \varepsilon_e)/2 \) 'seen' by the extraordinary magnetic dipole mode.

The spectra in Fig. 2(a) reflect the excitation of the higher-frequency ordinary magnetic dipole mode of a sphere of radius \( r = 10.7 \mu m \). In this case, the \( c \)-axis of TiO\(_2\) is strictly perpendicular to the incident field polarization plane, and the electric field of the magnetic dipole mode experiences only the ordinary component of the dielectric tensor, \( \varepsilon_o \).

Figure 4 illustrates the spectrum of the sphere of radius \( r = 15 \mu m \), in which the ordinary and extraordinary magnetic dipole modes are excited simultaneously. The ratio of the peak amplitudes is related to the in-plane angle \( \alpha_{XY} \) between the THz field polarization plane and the optical axis in the sphere. In the case of Fig. 4, its value was found to be equal to 50° via full-wave numerical simulations. Figure 5 shows the ordinary magnetic resonance mode for a sample of radius \( r = 19.5 \mu m \). The \( c \)-axis in this case is perpendicular to the field polarisation plane. In the same sample oriented at \( \alpha_{XY} = 45^\circ \), both magnetic dipole modes were detected (inset in Fig. 5).

The linewidths of the resonances extracted using the Fano profile fit (Eq. 1) to the experimental near-field data are presented in Table 1. As discussed earlier in Sec. 3.3, these near-field data give an upper limit for the intrinsic linewidth of such resonators. Thus, any dielectric resonators characterised using the present method are expected to exhibit even narrower resonances in free space.
We detected the splitting of magnetic dipole resonances we were able to excite either one of the modes or both of the highest observed values of the measured TiO$_2$ spheres, their Fano-model fitting parameters, and the estimated quality factors $Q_{F,o,e}$. The errors in $f_o,e$ and $\varepsilon_o,e$ are determined by the spectral resolution of 58 GHz for samples #1-3 and 29 GHz for sample #4. For sample #1, the radius was taken from its SEM image (inset, Fig. 2a). The radii of samples #2 and #4 were estimated using an optical microscope, which is less accurate as compared to SEM (+/-1um), and additionally adjusted within the error range via full-wave numerical simulations to match $\varepsilon_o = 70$ (taken as a reference value from sample #1). The radius of sample #3 was evaluated using a method similar to that for samples #1, #2, and #4 via the wave simulations. It could not be measured as sample #3 had fallen off the substrate and been lost. The errors in the radii of samples #2-4 are linked to the spectral resolution of the experiment.

Table 1 Measured and simulated characteristics of the studied TiO$_2$ spheres, their Fano-model fitting parameters, and the estimated quality factors $Q_{F,o,e}$. The errors in $f_o,e$ and $\varepsilon_o,e$ are determined by the spectral resolution of 58 GHz for samples #1-3 and 29 GHz for sample #4. For sample #1, the radius was taken from its SEM image (inset, Fig. 2a). The radii of samples #2 and #4 were estimated using an optical microscope, which is less accurate as compared to SEM (+/-1um), and additionally adjusted within the error range via full-wave numerical simulations to match $\varepsilon_o = 70$ (taken as a reference value from sample #1). The radius of sample #3 was evaluated using a method similar to that for samples #1, #2, and #4 via the wave simulations. It could not be measured as sample #3 had fallen off the substrate and been lost. The errors in the radii of samples #2-4 are linked to the spectral resolution of the experiment.

The quality factors $Q_{F,o,e}$ vary from one sample to another. We attribute this to the morphology of the micro-spheres. SEM images and XRD analysis of the studied and similar spheres indicate the presence of voids and inclusions of other crystal phases, which affects the level of losses experienced by the excited magnetic dipole modes. The highest observed values of $Q_F$ (≈ 90, sample #4) are comparable with the best experimentally reported $Q_F$ for Aluminium split-ring resonators at THz frequencies [28-30].

Both the ordinary and extraordinary permittivities for all samples were extracted from numerical simulations, except for sample #3. For the latter, the ordinary permittivity of TiO$_2$ was set equal to the value obtained for other samples and used to estimate the radius of the sample. The slight discrepancy in the values of the permittivities is most likely due to the material and geometrical variations of the measured TiO$_2$ micro-spheres.

Fitting analytical Fano-resonance curves to our measured data confirmed the extreme narrowness - tens of gigahertz of the observed magnetic dipole resonance peaks. This fact makes TiO$_2$ micro-resonators a promising base for THz all-dielectric metamaterials and resonance-based devices, such as detectors and filters.

4. Conclusions

We detected the splitting of magnetic dipole resonances in anisotropic TiO$_2$ spherical micro-resonators into ordinary and extraordinary modes using near-field THz time-domain spectroscopy. By changing the orientation of the samples with respect to the incident field polarization plane, we were able to excite either one of the modes or both of them simultaneously. We found that the near-field spectra are well described by the Fano-resonance model due to the underlying superposition of the modal fields and the incident standing wave formed behind the metallic screen of the near-field probe. By fitting the Fano-resonance model to the measured near-field spectra, we extracted the intrinsic properties of the studied anisotropic TiO$_2$ micro-sphere resonators. We show, that one can describe the near-field spectra of the anisotropic dielectric resonators by a superposition of two Fano lineshapes, weighted in accordance to the orientation of the samples with respect to the polarization plane of the incident THz pulse. Using full-wave numerical simulations, we estimated the ordinary and extraordinary permittivities of mono-crystalline TiO$_2$ a ≈ 70 and a ≈ 130, respectively. Linewidths as narrow as tens of GHz in magnetic dipole resonances at ≈ 1 THz suggest, that TiO$_2$ micro-resonators are promising candidates for all-dielectric THz metamaterials, non-reflective metasurfaces based on Huygens sources, and resonance-based devices, including detectors and filters.

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