



A case study: The negative THz time shift observed for Cu nanoparticle colloids

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ABSTRACT

We report a case study of the experimentally observed negative shift for the Copper nanoparticle colloids (NPs) when they are kept in contact with a quartz interface. This investigation is based on the previously reported measurements on various volumetric concentrations of Cu NPs using the Terahertz Time-Domain Spectroscopy (THz-TDS) technique. A gradually increasing negative time shift reminiscent of a superluminal propagation was observed for the Cu NPs in contrast with Ag NPs. In this work, we explain the possible reason for such observation by quantifying the recorded negative delays with high precision and by modelling the THz peak profiles under the assumption of a thin film formation at the dielectric colloid interface. Cu nanoparticle colloids with the same specifications were produced under the same conditions to verify the effect of the quartz interfacial layer. Quartz slides were kept immersed inside the colloids for up to 3 days and periodically monitored using UV-visible spectroscopy technique. While the Ag NPs did not show any evidence of thin film formation, the Surface Plasmon resonance absorption peaks were measured for Cu NPs, proving a thin layer formation on the slide surface. Our findings explain the advanced phase shift occurring at the dielectric-conductor interface which is valid only when the electromagnetic field transmits into the absorbing medium in the presence of a thin conducting layer.

1. Introduction

Nanoparticle production and characterization is a major field of interest with a broad range of potential applications in many scientific and industrial disciplines. The physical, chemical and electro-optic properties of materials are size-dependent and can be manipulated by controlling their size and shape [1]. While the characterization of isolated NPs is of fundamental interest, the NPs-Surface interactions, adhesion, contact mechanisms and their stability in solutions also play a key role in merging colloidal science and coating-based applications [2–5].

Terahertz Time Domain Spectroscopy (THz-TDS) has proven to be a safe and effective method for the characterization of bulk or even nanoscale materials with a major advantage of determining the absorption coefficient and the refractive index in connection with the amplitude and phase of the THz signal [6,7]. It is also important to note that, generally, in a THz-TDS system, measurements are not sensitive enough to discern an intensity change through nano- or sub-micron-thick films. For this reason, to measure changes in the THz amplitude due to THz absorption of the formation of a layer due to a colloidal system one

requires measurement with a relatively large path length [8,9]. As the thickness of the layers shrink to nano-scales, material and surface interactions become dominant, demanding careful attention when analysing metallic nanoparticle suspensions with phase-sensitive measurement techniques. This is because the total phase change and THz transmission are highly influenced by interface effects between different conducting media. Advancements in optoelectronics, for instance, are increasingly driven by the behaviour of novel materials, in thin film architectures such as perovskites, oxide metallics, and nanoparticles, where interfaces are critical for device performance [10]. Optimizing performance and ensuring long-term stability critically depend on understanding these interfacial properties, such as charge transport facilitated by new inorganic materials like copper oxide and advanced electron transport layers [11]. Indeed, a critical overview of thin film coating technologies for energy applications underscores the paramount importance of interfacial engineering [12]. These insights into thin film formation and complex interfacial dynamics are especially crucial for metallic nanoparticles, where surface adhesion and particle-substrate interactions significantly govern their properties and

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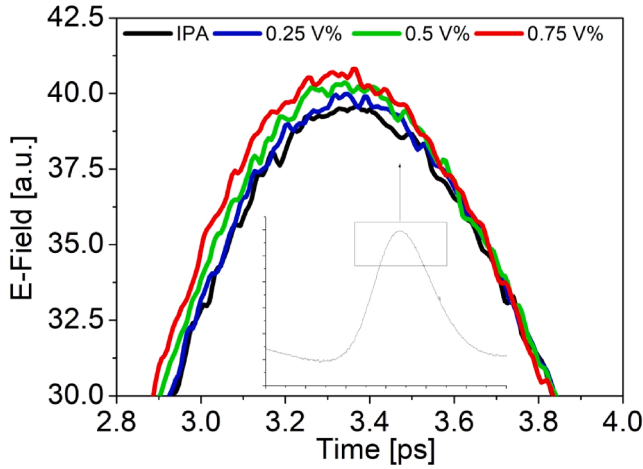


Fig. 1. THz time domain data through various colloids examined around the main peak of the THz signal. THz time domain signal of Cu-NPs and the reference host fluid (2-propanol) waveform is shown with the inset. The NPs ratio to the host medium is three-quarters (0.75 NPs), half (0.50 NPs) and one-quarter (0.25 NPs) by volume consecutively. The data is recovered by permission.

behaviour. Our work on the negative THz time shift in copper nanoparticle colloids exemplifies this, demonstrating how nanoparticle adhesion, leading to a thin conducting layer at a dielectric-conductor interface, fundamentally alters THz pulse propagation and provides a key case study of these interface effects.

While THz-TDS is a powerful tool for material characterization, the observation of a negative time shift, indicating an earlier arrival of the THz pulse, is a relatively rare phenomenon in studies of conventional materials. Such advanced phase shifts have been noted in certain advanced materials and systems, however, a comprehensive investigation and a clear, unified explanation for this intriguing behaviour, particularly concerning nanoparticle colloids and their interactions at interfaces, remains underexplored. This study is precisely motivated by this gap in understanding, aiming to provide a thorough analysis and a robust explanation for the negative THz time shift observed in copper nanoparticle colloids, shedding light on the underlying physical mechanisms governing electromagnetic wave propagation at critical material interfaces.

In this work, we focus on understanding the dynamics behind the observed negative shift for Cu-NPs when kept in contact with a quartz interface. The observed negative shift, obtained by measuring the phase of the THz pulse the interface, indicates that the THz pulse appears to arrive earlier than anticipated when passing through the sample. This case study is based on the previously reported measurements on various volumetric concentrations of nanoparticle colloids performed by using the THz-TDS technique [13] (Fig. 1). Here, the Cu-NPs colloids show a similar behaviour with the Ag-NPs with similar sizes such that, the power absorption coefficient and the refractive index showed no discernible difference between the reference host fluid and the colloids when analysed across the entire THz spectrum. On the other hand, the time-domain profiles show notable differences such as a slight increase in amplitude supported by a negative time shift. At first, this behaviour looked similar to superluminal propagation through the layered medium, however in fact the negative shift and slight decrease in amplitude can be explained if one assumes that the THz beam is sensing the concentration of Cu nanoparticles near the first and second interface (quartz and Cu NPs suspension) in the form of a very thin conducting layer, which advances the phase of the THz pulse. This phenomenon was also reported for photo-excited materials as probed by terahertz transients [14,15] where a negative phase shift is observed and correctly attribute to non-superluminal propagation. In this work, first the background

based on thin film formation at the interfaces is given. The measured shifts are quantified with higher precision by modelling the observed THz signal peak profiles near the main peak of the signal transmission through the NP colloids assuming layers that are formed at the interfaces. This assumption in the model is supported by UV-visible spectroscopy techniques which show the formation of a thin film made up of Cu NPs at the quartz interface. The use of both THz and UV-visible experimental techniques support the model and fully explain the observed effect, in terms of a frequency-dependent transmission and phase shift at the dielectric-conductor interface, that this is not a superluminal propagation of the THz pulse..

1.1. Theory

For the general case of an observed positive shift, i.e. a time delay of the signal through sample, the sample characteristics can be extracted using a transfer function through multiple layers derived from the Fresnel transmission coefficients [16]. On the other hand, for the observed negative time shift, the frequency-dependent transmission and phase shift at the dielectric-conductor interface in connection with multilayers should be considered. The characteristic matrix for a time-harmonic electromagnetic wave propagating through a stratified medium can be derived from Maxwell's equations. Detailed derivations are given in the References [17,18]. When a plane wave of angular frequency ω is transmitted through an absorbing film, index of refraction n_2 with the corresponding field absorption coefficient α_2 , which is in between two dielectric media with refractive indices n_1 and n_3 , the field phase shifts at the first and second interfaces, respectively, are given by:

$$\tan \chi_{12} = -\frac{\frac{\alpha_2 c}{\omega}}{n_1 \cos \theta_1 + n_2} \quad (1)$$

$$\tan \chi_{23} = \frac{\frac{\alpha_2 c}{\omega} n_3 \cos \theta_3}{n_2^2 + \left(\frac{\alpha_2 c}{\omega}\right)^2 + n_2 n_3 \cos \theta_3} \quad (2)$$

Where the subscript 1–2 refers to the first interface as the electromagnetic wave passes from dielectric (quartz) to a conducting (thin film) medium. The subscript 2–3 refers to the second interface from the conducting medium into the dielectric (colloid) medium. As seen in Eq. (1), the negative phase shift of the field is caused by the dielectric-conductor interface as an electromagnetic field is transmitted into an absorbing medium. Since the interface from the conducting medium into the dielectric medium does not affect the negative shift, the film formation on the second wall of the quartz cuvette is not considered for the phase shift. Furthermore, as the THz beam is highly absorbed by the polar fluids, the possible resulting internal reflections were not detectable.

This observation suggests that the THz beam is sensing the concentration of nanoparticles near the first and second interface (quartz and absorbing NPs) as a very thin layer. Conversely, due to the large path length (2 mm) of the cuvette, contrary to this, a predominantly positive shift would have been observed upon transmission as was observed for Ag NPs [19].

To accurately determine the frequency-dependent optical properties and precisely quantify the observed time shifts, the raw THz time-domain signals from both the reference (pure isopropanol) and the sample (NPs colloids) are first processed. These time-domain waveforms, $E_{\text{reference}}(t)$ and $E_{\text{sample}}(t)$, are converted into their respective frequency-domain spectra, $E_{\text{reference}}(\omega)$ and $E_{\text{sample}}(\omega)$, using a Fast Fourier Transform (FFT). From these complex spectra, the complex transmission function is calculated as the ratio of the sample spectrum to the reference spectrum: $H(\omega) = E_{\text{sample}}(\omega)/E_{\text{reference}}(\omega)$. This complex function inherently contains both the amplitude attenuation and the phase shift introduced by the sample. The magnitude $|H(\omega)|$ provides the frequency-dependent amplitude transmission, while the argument $\phi(\omega)$

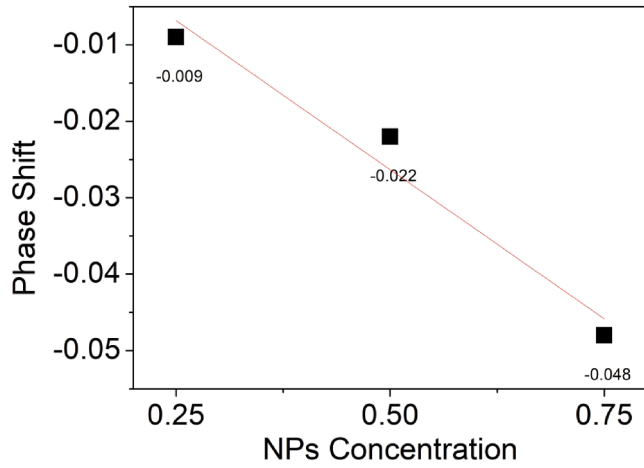


Fig. 2. Concentration-Dependent Phase Shift of THz Signal in Cu Nanoparticle Suspension at 0.5 THz.

$= \arg(H(\omega))$ yields the frequency-dependent phase shift.

For the precise estimation of the frequency-dependent phase shift and the consequent time-domain peak shift, we employed an iterative fitting procedure, as detailed in reference [19]. This method involves inverse transforming the frequency-dependent THz transmission signal through the medium into the time domain. An appropriate phase shift is then iteratively applied to the transformed isopropanol THz time-domain signal until the inverse transform of this modified waveform precisely matches the observed THz time-domain waveform of the nanoparticle suspension. This approach allows for a robust determination of the phase shift, even for subtle changes that manifest as shifts in the THz pulse peak in the time domain, thereby directly addressing the peak position and phase shift for various colloids.

We have recovered the data at 0.5 THz where the signal-to-noise ratio is maximum. The results have shown an almost linear trend of negative phase shifts with the concentrations as shown in Fig. 2. The higher concentration colloids are prone to form thicker films at the interface giving a relatively stronger negative time shift corresponding to the observed negative phase shift. Moreover, as the NPs inside the suspension start to form a thin film by aggregation at the quartz interface, we observe an increase in the THz intensity as a result of the higher rate of sedimentation and aggregation leaving a less dense suspension.

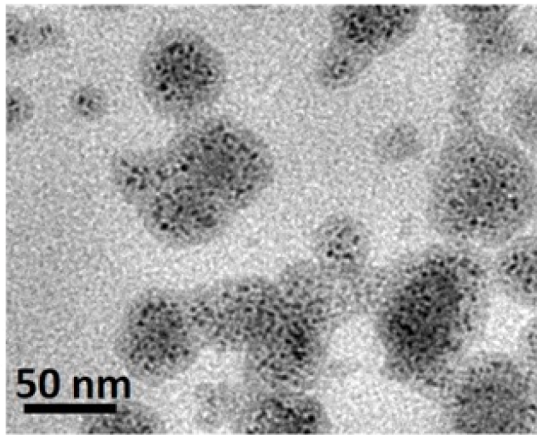
2. Materials and methods

To strengthen our hypothesis on the origin of the negative shift, Cu NP colloids were produced under the same conditions that were used for the THz measurements. Transmission Electron Microscopy (TEM) images of the synthesized Cu NPs is presented in Fig. 3(a). Nanoparticles were produced by pulsed laser ablation (PLA) in isopropanol host media. Their predominant average particle size was 10 nm, and the size distribution, presented in Fig. 3(b), was characterized by measuring the approximate diameters of 70 particles from TEM images using ImageJ software.

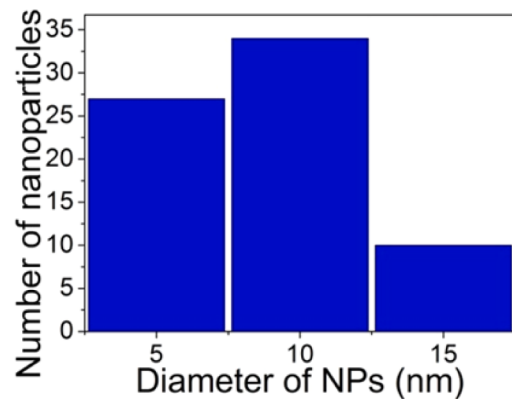
Colloids with the same volumetric concentration (as reported in the previous study) were divided into two quartz cuvettes. A quartz slide was immersed inside one of the cuvettes and both cuvettes were kept under the same ambient conditions for 3 days. Afterwards, the UV-visible spectrum of the Cu NPs suspension and the quartz slide immersed in the second cuvette were measured consecutively (Agilent, Cary 100 UV-Vis). The quartz slide was washed 3 times in a 2-propanol bath before the UV-visible absorption measurements. As shown in Fig. 4. The SPR (surface plasmon resonance) absorption peaks of the Cu nanoparticles are clearly observed, proving the formation of the Cu film at the suspension and the cuvette interface after being immersed for 3 days.

Furthermore, since this negative shift behaviour was not observed for the Ag NPs as reported previously, a similar experiment was done to study these colloids as shown in Fig. 5(a). In this context, Ag NPs using PLA (Pulsed Laser Ablation) were produced inside the 2-propanol matrix. Contrary to the Cu NPs suspension, the Ag NPs did not show any evidence of thin film formation on the quartz slide surface.

The absence of a significant absorption signal in the UV-visible spectra for the quartz slide immersed in Ag NPs, as depicted in Fig. 5 (a), is a critical observation. This clearly demonstrates that, unlike the Cu NPs (Fig. 4), the Ag nanoparticle solution did not adhere to the surface, thereby confirming the absence of thin film formation. This crucial distinction is further emphasized by the comparative UV-visible spectra presented in Fig. 5(b), which starkly highlights the differing interfacial behaviours between Ag NPs and Cu NPs. This direct experimental evidence strengthens our assertion that the negative THz time shift observed in Cu nanoparticle colloids is indeed a consequence of the formation of a thin conducting layer at the dielectric-conductor interface, a phenomenon not observed with Ag NPs due to their distinct adhesion properties.



a)



b)

Fig. 3. a) Transmission Electron Microscopy images of the synthesized Copper nanoparticles, showing their size and morphology, b) Nanoparticle Size distribution measured from TEM images.

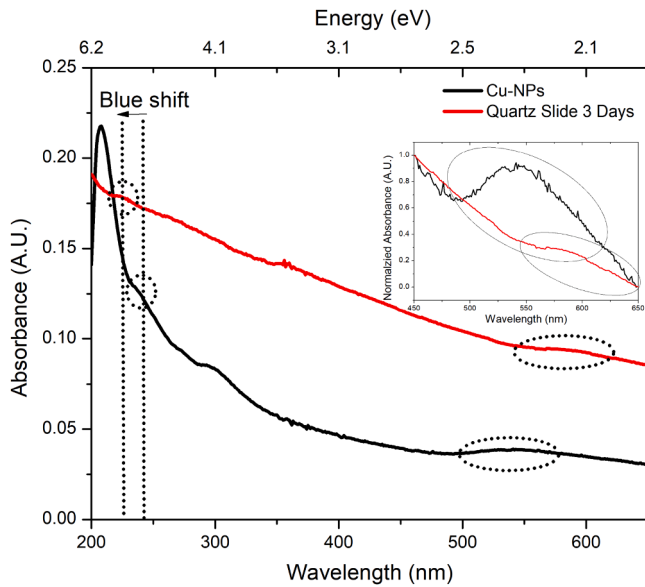
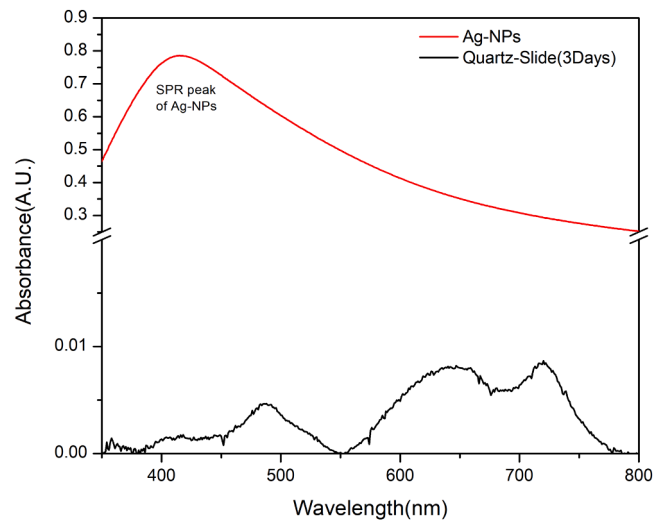


Fig. 4. The UV-visible spectra for the Cu NPs in comparison with the quartz slides embedded into the suspension sets. The normalized absorbance spectrum is shown in the inset, evidencing the SPR peaks of the Cu observed at the cuvette interface after being immersed for 3 days.

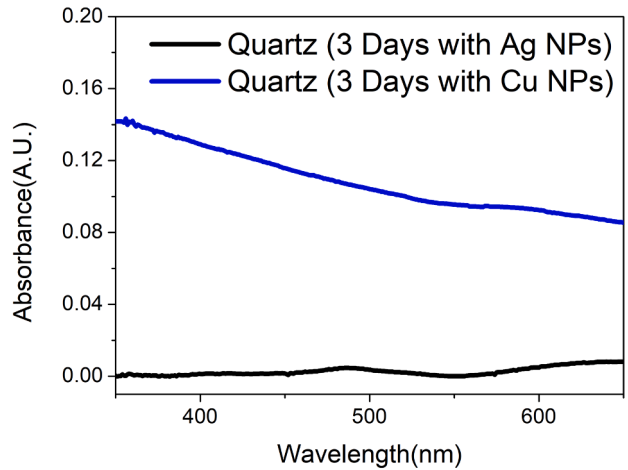
3. Results and discussion

The main purpose of the conducted work was to have a deeper understanding of the diverse terahertz response observed (a negative time shift recorded in the presence of Cu NPs which was not detected for Ag NPs) during the NPs investigation. This work specifically addresses the underexplored phenomenon of negative THz time shifts in nanoparticle colloids, providing a comprehensive explanation for this rare observation.

As a case study, the THz signal phase response through the stratified medium is modelled. The findings, suggest a thin layer formation on the inner surface of the quartz cuvette used during the measurements leading to a negative phase shift in accord with the modelled propagation of the THz field through a dielectric-conductor interface. The evidence of this interfacial conducting layer is experimentally investigated at the quartz interface using UV-visible spectroscopy techniques to understand plasmonic responses. By preparing a twin set of NPs, Cu NPs and Ag NPs, with the same specifications as were used in the previously reported works, the quartz interface was examined for layer formation [13,19]. While Cu NPs suspensions shown an adhesive behaviour forming a thin coating, the Ag NPs did not show any evidence of thin film formation on the quartz slide surface, supporting the model. These findings also demonstrate that the mechanisms for nanoparticle adhesion between Ag and Cu are different. In the literature, there has been extensive research on the mechanical properties of NPs in terms of the adhesion properties onto solid surfaces as a key element to coating-based advanced applications. It is a well-known concept that the shear modulus increases with the conductivity [20–22]. To this concern, Silver being a better conductor concerning copper, probably attains a higher shear modulus. It is important to note that, the adhesion properties of NPs are also dependent on the nanoparticle's shape and dimensions. Since the NPs used in this study were similar in shape and dimensions, one should take into consideration the diversities in the substrate-particle interactions. For instance, Carrillo et.al have reported the modelled dependence of the nanoparticle shape on the strength of the long-range van der Waals interactions with the substrate and the particle shear modulus [23]. Their findings show that, for NPs with large shear modulus, the increase in substrate-NP interaction strength results in small particle deformations leading to surface-phobic interactions.



a)



b)

Fig. 5. a) The UV-visible spectra plots for the Ag NPS in comparison with the quartz slides embedded into the suspensions. b) The comparative UV-visible spectra of quartz slides immersed in Ag NPs and Cu NPs, highlighting the absence of thin film formation for Ag NPs.

Moreover, the theoretical results also show that by increasing the substrate-NP interaction strength and decreasing the value of the shear modulus, the elastic energy penalty decreases and results in high affinity to the substrate. Studies reported in the literature regarding the shear modulus and adhesion properties of NPs onto solids coincide with our findings on the thin film formation diversities between Ag and Cu nanoparticles. This study as described here demonstrates that phase change based THz measurements can be successfully used to study conducting coatings and the adhesion properties of NPs.

In conclusion, the observed negative shift in THz pulse propagation, manifesting as an earlier arrival, is directly attributed to an advanced phase of the THz pulse. This phenomenon arises from the interaction of the THz beam with a very thin conducting layer formed by Cu nanoparticles at the dielectric-conductor interface, a finding strongly supported by experimental UV-visible spectroscopy results, which confirmed thin film formation on quartz surfaces by Cu but not Ag nanoparticles. This effect, distinct from superluminal propagation, represents a unique characteristic of electromagnetic wave transmission into an absorbing medium in the presence of such an interfacial conducting layer. This study underscores the high sensitivity of THz-TDS in

characterizing subtle material interfaces and thin film formations, offering a comprehensive explanation for the negative time shift based on these interfacial effects.

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Data availability statement

Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

Conflicts of interest

The authors declare no conflict of interest.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work the authors used “JENNI.AI” service in order to improve language and readability. After using this tool, the authors reviewed and edited the content as needed and takes full responsibility for the content of the publication.

CRediT authorship contribution statement

Can Koral: Writing – original draft, Visualization, Validation, Software, Investigation, Formal analysis, Data curation, Conceptualization. **Bülend Ortaç:** Writing – review & editing, Visualization, Validation, Resources, Investigation, Formal analysis, Data curation. **Hakan Altan:** Writing – review & editing, Visualization, Validation, Resources, Investigation, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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