Quantitative Analysis of Metal Particles Concentration in the Composites Based on Terahertz Linear Scatter Method

Zhangfan Yang, Qichao Wang, Ziyang Cao, Xianying Wang, and Yan Peng

***Abstract*—Adding metal particles into the material is an effective method to improve the physical and chemical properties of nonpolar materials. However, the concentration of metal particles inside material cannot be adequately measured through conventional methods, such as scanning electron microscope or optical microscope. In this article, based on terahertz time-domain spectroscopy (THz-TDS) system, we propose a "Terahertz Linear Scatter" method to realize the quantitative analysis of metal particles concentration in nonpolar materials. Taking the composite graphene-nanosilver film as an example, THz wave can penetrate graphene with high transmittance, while it will be effectively scattered by nanosilver particles. Importantly, the small volume of the metal particles makes the attenuation of received signals change in a linear fashion. Based on this principle, the concentration of metal particles in nonpolar materials can be identified rapidly and accurately. The corresponding determination coefficient R^2 can be as high as 0.9669. These results are of great significance for the analysis of various materials containing metal particles.**

***Index Terms*—Metal particles concentration, quantitative analysis, terahertz time-domain spectroscopy (THz-TDS), terahertz linear scatter.**

I. Introduction

IN RECENT years, the method of adding metal particles into nonpolar material has been greatly developed. In the aspect of material performances, adding metal particles into composite can improve its physical and chemical properties. For example, combining the bridging effect of silver nanowires with chemical doping method can significantly enhance the electrical conductivity of graphene films grown by chemical vapor deposition [1]. In the aspect of material detection [2], [3], nanosilver particles can be added in multilayer graphene to improve surface-enhanced Raman scattering effect. In the aspect of biomedical research, nanosilver-based composites can be inserted into the medicines for treating burn wounds of human skin, which can effectively kill bacteria, decrease infection, and promote therapeutic effect [4], [5]. However, for the concentration detection of metal particles in composites, traditional methods such as scanning electron microscope (SEM) and optical microscopic [6] can only observe the metal particles located on the surface of the composites, whereas the metal particles inside the composites cannot be detected. Therefore, the accurate analysis and further application for the material properties will be affected. In addition, the feasible detection methods for metal particles inside material, such as inductively coupled plasma optical emission spectrometry [7], nuclear magnetic resonance, and X-ray powder diffraction (XRD) [8], requiring complex pretreatment, which is time-consuming, inefficient, and expensive. Terahertz (THz) wave is electromagnetic radiation [9] with frequency ranging from 0.1 to 10 THz, which is located between microwave and infrared waves. It has many unique features, including high resolution, spectral fingerprinting, large bandwidth, low photon energy, and also high penetration for nonpolar materials [10]. Therefore, THz wave has many potential applications in the fields of materials [11]–[13], biology [14]–[17], safety inspection [18], [19], communication [20], and imaging [21], [22]. In this article, based on Rayleigh scattering theory and terahertz spectroscopy (THz-TDS) system, we propose a "Terahertz Linear Scatter (TLS)" method to realize the quantitative analysis of metal particles concentration in materials. Considering the different penetrability of THz wave for nonpolar material and metal particles, the higher the metal particles concentration, the more signal will be scattered, and then the weaker the terahertz transmission signal is. Based on this principle, the quantitative relation between concentration of metal particles and THz transmission signal can be established, and the metal particles concentration in materials can be accurately detected. The TLS method that delivered in this article has advantages of accuracy, convenience, and rapidity.

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II. Method and Discussion

As a first step, a database should be set, which is of correspondence relation between the concentration of metal particles in the composites and the transmission signal amplitude of THz wave. Then, for the unknown samples, the metal particles concentration can be obtained rapidly by using this database.

According to the definition of Rayleigh scattering, when a beam meets a particle whose diameter is much smaller than the wavelength of it, the beam will be scattered in all directions, and the intensity of scattering is proportional to the fourth power of the light wave frequency [23]. The wavelength of THz wave is about submillimeter scale. Therefore, when THz wave penetrates the nonpolar material containing nano/micrometer level metal particles, the Rayleigh scattering effect determines that only part of the beam can penetrate the sample and be received by the detector. In addition, the higher the concentration of metal particles, the lower the transmitted THz amplitude is.

Considering polyethylene (PE) has little absorption for THz wave [24] during the frequency range of 0.1–3.0 THz, it is chosen as the base of composite in the experiment, and nanosilver particles are chosen as metal particles to dope in the composite. Nanosilver particles are purchased from Sigma-Aldrich Company, whose average diameter is ∼100 nm. To avoid the agglomeration of particles, there are already some PVP dispersant contained in it, which is transparent in the THz band and therefore no effect for the final concentration analysis. We mixed PE powder with nanosilver particles powder evenly under different proportions, then made the mixed powder into round tablets with the thickness of 1 ± 0.05 mm and diameter of 13 ± 0.05 mm. The errors are mainly caused by handmade tablets and the signal jitter of THz-TDS, which can be improved by optimizing the preparation process. These tablets are detected by a THz-TDS system [25]. For this system, the diameter of optical beam is ∼2 mm, the diameter of the THz beam is ∼13 mm, the spectral resolution is 15 GHz, and signal to noise ratio (SNR) is over 1000:1. In the experiment, nitrogen was injected into the sample chamber, so that the humidity in the sample chamber was reduced to ∼3%, and the temperature in the chamber was ∼20 °C.

An independent test was designed to confirm the accuracy of the experiment. To ensure the highest resolution of our method about distinguishing samples with different concentrations, eight tablets are made with the concentration of 1.0%, 1.2%, 1.4%, 1.6%, 1.8%, 2.0%, 2.5%, and 3.0%. To make sure the stability of tests, we prepared five samples for each concentration (one group), and every sample was tested for five times to get the corresponding error bar.

By setting these groups, the lower limit and interval for the metal particles concentration detection can be accurately identified. The THz amplitude change as a function of the metal particles concentration are shown in Fig. 1.

Fig. 1(a) shows the THz time-domain spectra of eight sample groups with different concentrations. Each adjacent spectrum is horizontally offset 5 ps for distinction. It can be seen clearly that the THz amplitude decreases with the increase of sample concentration. The corresponding linear relation between the concentration and THz amplitude is plotted in Fig. 1(b). By analyzing the linearity and error range, we found that the THz-TDS measurement can distinguish ∼0.6% concentration difference of metal particles (by comparing the maximum and minimum of amplitudes under different concentration cases). For this limitation, the concentration resolution of the experiment can be further improved if the errors from sample fabrication and the system chattering can be technically reduced.

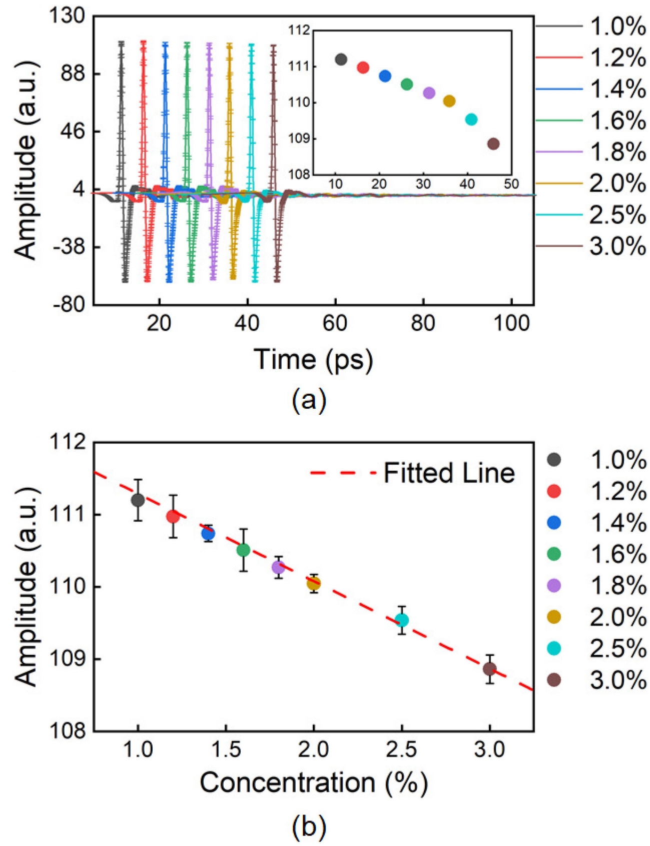

Fig. 1. (a) THz time-domain spectra of five groups samples with different concentrations (1.0%, 1.2%, 1.4%, 1.6%, 1.8%, 2.0%, 2.5%, and 3.0%). The corresponding error bars have been labeled and the partial enlarged drawing is shown as the inset. (b) Linear relation between THz spectral amplitude and actual concentrations. The circle dots are the experimental data and the red dotted lines are the linear fitting.

Next, we built the database used for concentration identification. In order to ensure the adequacy of database, we prepared 16 groups of samples, each group contains five PE-nanosilver composite samples with the same concentration. The concentrations of 16 groups of samples include 1%, 3%, 5%, 7%, 9%, 11%, 13%, 15%, 17%, 19%, 21%, 23%, 25%, 27%, 29%, and 31%. Each sample contained 100 mg PE powder as the base, and the accuracy of concentration is ∼0.2%. The reference tablet was made of 100 mg PE powder and its THz detected signal was used as the background signal. Then, 16 groups of composite tablets were detected to acquire their THz time-domain waveforms. The waveforms with the corresponding error bars are shown in Fig. 2(a).

By linear fitting for the nanosilver particles concentration and corresponding peak amplitude of THz time-domain spectra,

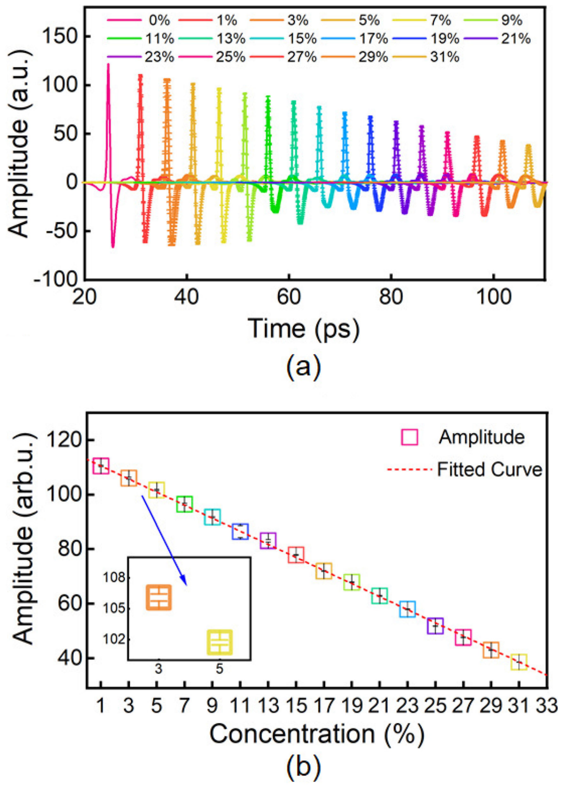

Fig. 2. (a) Time-domain spectra of samples with different concentrations of 1%, 3%, 5%, 7%, 9%, 11%, 13%, 15%, 17%, 19%, 21%, 23%, 25%, 27%, 29%, and 31%. Each adjacent curve was horizontally offset 5 ps for distinction. (b) Linear fitting for the silver particles concentration in sample and the corresponding THz amplitude. The corresponding error bars have been labeled and the partial enlarged drawing is shown as the inset.

the database can be obtained effectively [see Fig. 2(b)]. It can be seen clearly that the peak amplitudes of THz transmission signals present a good linear change as a function of the metal particles concentration. We deduce that the small volume of the metal particles (nanoscale) make the scatter effect and signal attenuation change very steadily, resulting in the final signal change in a linear fashion. According to the linear relation between the peak amplitudes of THz transmission signals and nanosilver particles concentration of the composite, it can be proved that once the THz transmission signal is detected, the metal particles concentration of composite can be calculated immediately.

It should be noticed that various materials have different transmissivity to THz wave, which can result in different background signal. Therefore, curve in Fig. 2(b) cannot be used directly when the PE powder is replaced by other nonpolar materials as the base of samples. In order to use this curve to analyze the metal particles concentration in other nonpolar materials, we set a formula to define the relation between PE and other nonpolar materials

$$A_{0T} = (A_0 - A_S) + A_X. \tag{1}$$

And the corresponding linear equation is

$$C_{0T} = (113.16 - A_{0T})/2.41. \tag{2}$$

In formula (1), A_0, A_S, and A_X are the THz transmission signal amplitudes of pure PE tablet, pure nonpolar material, and composite mixed by nonpolar material and metal particles, respectively. A_{0T} is corresponding value of transmission signal amplitude that can be used in the database. In formula (2), C_{0T} is the concentration of metal particles in composite, 113.16 and 2.41 are the parameters of linear equation calculated according to Fig. 2(b). Based on formulas (1) and (2), once A_S and A_X are detected by THz system, the metal particles concentration in these composites can be obtained quickly and accurately.

III. Result and Discussion

To verify the effectiveness of our quantitative measurement and analytical method, a material with high transmittance for THz wave should be chosen for test.

Graphene is a two-dimensional material with excellent physical and chemical properties. It is often used to prepare functionalized materials by combination with metal particles.

Therefore, in the experiment, the pure multilayer graphene film [24] and the multilayer graphene-nanosilver particles composite films were chosen as the test groups. The multilayer graphene-nanosilver films were fabricated by vacuum filtration method, the graphene solution (0.5 mg/ml) was made by electrochemical method, and nanosilver solution (0.1 mg/ml) was made by chemical reduction method. The volume ratios of graphene to nanosilver solution are 4:1, 2:1, 1:1, respectively. These films were all uniformly prepared as round films with thickness of 1.3 ± 0.2 μm and diameter of 13.2 ± 0.5 mm to eliminate the influence of thickness and shape on THz transmission amplitude. SEM was used to characterize the morphology of the multilayer graphene-nanosilver particles composite films. The corresponding top and cross-sectional SEM images of these films were shown in Fig. 3(a) and (b).

The distribution of nanosilver particles on the composite film surface can be seen clearly, whereas the nanosilver concentration inside of the films cannot be quantitatively analyzed. Here, by using the THz-TDS system, the pure and composite multilayer graphene films were detected. As shown in Fig. 3(c), the black curve is time-domain spectra of pure multilayer graphene film, and the other three curves (red, blue, and green) are the time-domain spectra of three composite multilayer graphene-nanosilver particles films with different concentrations. The corresponding error bars of measurements are also labeled on them. The amplitudes of pure multilayer graphene film and composite multilayer graphene-nanosilver particles films are used as As and Ax in Eq. (1), respectively. By taking use of the Eq. (1) and Eq. (2), and database Fig. 1(b), the concentration of metal particles in graphene-nanosilver composite films can be theoretically predicted [Fig. 3(d), red circles]. The actual fabricated concentrations of nanosilver particles in these three composite films are 5.04%, 10.08%, and 20.17%, respectively, and the detection results of these three films are 4.92%, 10.13%, and 20.30%, respectively. As shown in Table I, the determination coefficient of our TLS method R^2_{TLS} reaches 0.9669. These results prove the effectiveness and accuracy of the method.

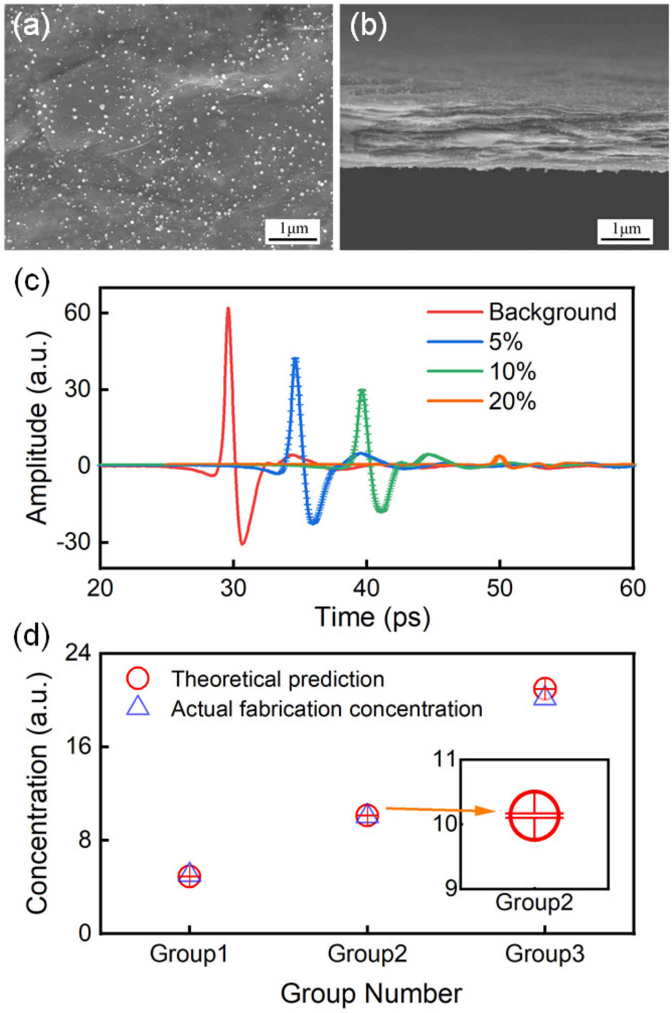

Fig. 3. (a) The top-sectional SEM image of graphene-nanosilver particles composite film. (b) The cross-sectional SEM image of graphene-nanosilver particles composite film. (c) Time-domain spectra of three multilayer graphene-nanosilver composite films with different nanosilver concentration. The corresponding error bars of measurements are also labeled on them. (d) Peak amplitude of transmission signal as a function of the nanosilver particles concentration. These red circles are theoretical prediction and the blue triangles are the actual fabrication concentration. The corresponding error bars have been labeled and the partial enlarged drawing is shown as the inset.

TABLE I
ERRORS BETWEEN THEORETICAL PREDICTION AND ACTUAL FABRICATION CONCENTRATION IN TLS METHOD

Actual fabrication concentration (%)	Theoretical prediction (%)	R^2_{TLS}
5.04	4.92	
10.08	10.13	0.9669
20.17	20.30	

For comparison, we also tested these three groups of samples by traditional XRD method. The corresponding result is shown in Fig. 4. According to "Collection of Simulated XRD Powder Patterns for Zeolites" [26], we can find that the peaks of number 1 and 5 match the diffraction peak of graphene, the peaks of number 2, 3, 4, and 6 match the diffraction peak of nanosilver particles. By extracting the diffraction peaks area of nanosilver particles from the XRD spectra in Fig. 4, we also calculate the determination coefficient of XRD method R^2_{XRD}, as shown in Table II.

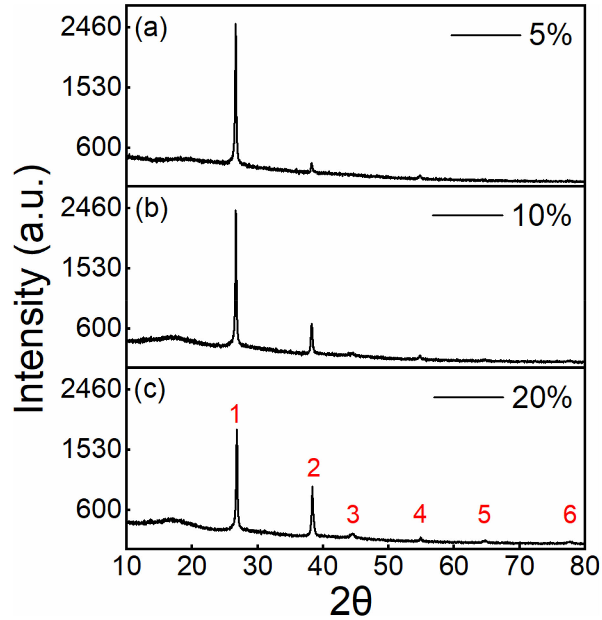

Fig. 4. XRD spectra of three multilayer graphene-nanosilver composite films, which are consistent with the samples in Fig. 3.

TABLE II
ERRORS BETWEEN THEORETICAL PREDICTION AND ACTUAL FABRICATION CONCENTRATION IN XRD METHOD

Actual fabrication concentration (%)	Theoretical prediction (%)	R^2_{XRD}
5.04	6.87	
10.08	15.73	0.5756
20.17	24.42	

It can be seen that the value of R^2_{XRD} is only 0.5756, which means the theoretical prediction by XRD has a large error and poor relation with the actual concentration. XRD is a method of detecting the signal obtained by X-ray diffraction in crystals. However, in the process of sample preparation, uncontrollable factors such as preferred orientation of crystal arrangement and damage of crystal structure will inevitably exist, which will lead to unstable diffraction peak strength, causing large error in quantitative analysis of sample concentration. Therefore, the XRD method can only be used for the semiquantitative analysis.

IV. CONCLUSION

We proposed a "Terahertz Linear Scatter" method for quantitative analysis of metal particles concentration in composites. By using THz-TDS system and establishing a linear relation between the metal particles concentration and the THz transmission amplitude, the metal particles concentration in nonpolar materials can be obtained accurately and rapidly. Moreover, because of the weak ionization property, THz wave will not cause damage to materials during the detection. Therefore, "Terahertz

Linear Scatter" method provides a new and efficient view for the field of internal information detection of substance.

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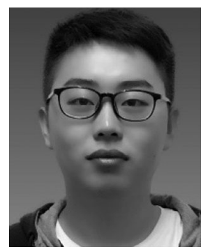

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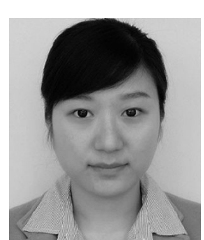

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