Front. Phys. 12(3), 124205 (2017)
DOI 10.1007/s11467-017-0673-y

Research article

Spectral blueshift as a three-dimensional structure-ordering process

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Received October 10, 2016; accepted January 4, 2017

The transmission spectra of a TiO_2-silicone oil suspension in an increasing external electric field are studied. As the electric field increases, the structure of the suspension changes from a disordered one to an ordered one. Interestingly, the transmission spectra blueshift in this structure-ordering process. Furthermore, the relative transmission spectra exhibit Fano-like asymmetric line shapes. The deviation ratio of each asymmetric line shape increases monotonously as the disorder of the suspension decreases. We suggest that this blueshift phenomenon can be used to characterize the disorder strength of three-dimensional systems.

Keywords disordered medium, light propagation, transmission spectrum, blueshift

PACS numbers 42.25.Bs, 2.25.Dd

1 Introduction

Light propagating in random media undergoes multiple scattering, which, in general, can be described as a diffusive process [1]. However, in periodic materials, the ballistic process caused by Bragg scattering governs the propagation of light [2]. The difference between these two scattering processes is the presence of disorder, which changes the periodic potential of an ordered structure to a random one. The effects of disorder on transmittance versus sample thickness [3–6], shape of light speckles [7–11], internal optical intensity distributions [12–15], propagation of light pulses [15–18], and transmission spectra [14, 15, 19–23] have been studied extensively through experiment and simulation.

During the change in structure from a disordered one to an ordered one, the diffusive transport caused by multiple scattering shifts to ballistic transport caused by Bragg scattering. The competition and interference of light between these two scattering processes lead to the occurrence of many novel optical phenomena [7, 19, 24–27]. The interplay between order and disorder has become an active research topic, which is yet to be completely explored [3, 7–10, 20, 21, 26, 27]. Here, we report experimental observations of the transmission spectra of a TiO_2-silicone oil suspension as its three-dimensional (3D) structure was changed from a disordered one to an ordered one. Interestingly, these transmission spectra blueshifted during the structure-ordering process. Furthermore, the relative transmission spectra exhibited Fano-like [28] asymmetric line shapes. The deviation ratio of each asymmetric line shape increased monotonously as the disorder decreased. We suggest this analogous Fano effect can be used to characterize the disorder strength of 3D systems.

2 Experiment and discussion

We studied the transmission spectra of a suspension comprised of dielectric particles in an increasing direct current (dc) electric field. The dielectric particles used were of titanium oxide (TiO_2; DuPont, Wilmington, DE, USA, R902), with an average particle diameter of 405 nm. The high refractive index of 2.7 and large bandgap of 3.0–3.2 eV [29] make TiO_2 particles a highly suitable material for the study of light propagation in random media [16, 18]. The TiO_2 particles were suspended in transparent dimethyl silicone oil (Sinopharm GmbH, Schleswig-Holstein, Germany, H201, 50 $mm^2{\cdot}s^{-1}$), at a total volume fraction of ∼34%. The refractive index of silicone oil is ∼1.4, which is much smaller than that of TiO_2 particles. This disparity between the refractive indices ensured multiple scattering in the suspension.

Brownian motion causes the TiO_2 particles to disperse randomly in the TiO_2-silicone oil suspension. When an external electric field is applied, the TiO_2 particles in the suspension become polarized [Fig. 1(a)] and gather to form chains [Fig. 1(b)] along the direction of the electric field [30]. As the electric field increases, the short chains connect to form long chains and eventually, columns [30], which have an ordered body-centered-cubic structure [31]. Thus, the structure of a TiO_2-silicone oil suspension undergoes ordering in an increasing electric field.

The TiO_2 suspension was carefully injected into a cuvette, which was made by ITO glass and had a rounded 20 mm-diameter outer surface and its parallel inner conductive surfaces were 1 mm apart. An external DC electric field E was applied to the suspension through charging the inner conductive surfaces. Supercontinuum white laser light (NKT Photonics, Birkerød, Denmark, Super Extreme), with an average spot diameter of 1 mm, propagated through the cuvette with the wave vector $\boldsymbol{k}//\boldsymbol{E}$, and was recorded by a spectrometer (Ideaoptics, Shanghai, China, PG2000-pro) with a 1.4 nm wavelength resolution. Figure 2 shows the remarkable blueshift in the transmission spectra of the TiO_2 suspension in an electric field as the electric field increased. The blueshift was a few nanometers.

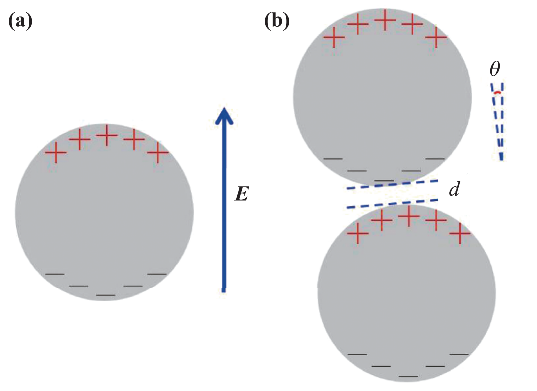

Fig. 1 Dielectric particles (spheres) in an external electric field (direct current). **(a)** The particles are polarized by the electric field. **(b)** The polarized particles gather to form chains. As the electric field increases, the gap d between neighboring particles decreases, as does the angle of deviation, θ, between the chains and the electric field.

We investigated the blueshift of the transmission spectra using the relative transmission spectra shown in Fig. 3. These spectra were obtained by scaling each TiO_2 suspension transmission spectrum using the same sam-

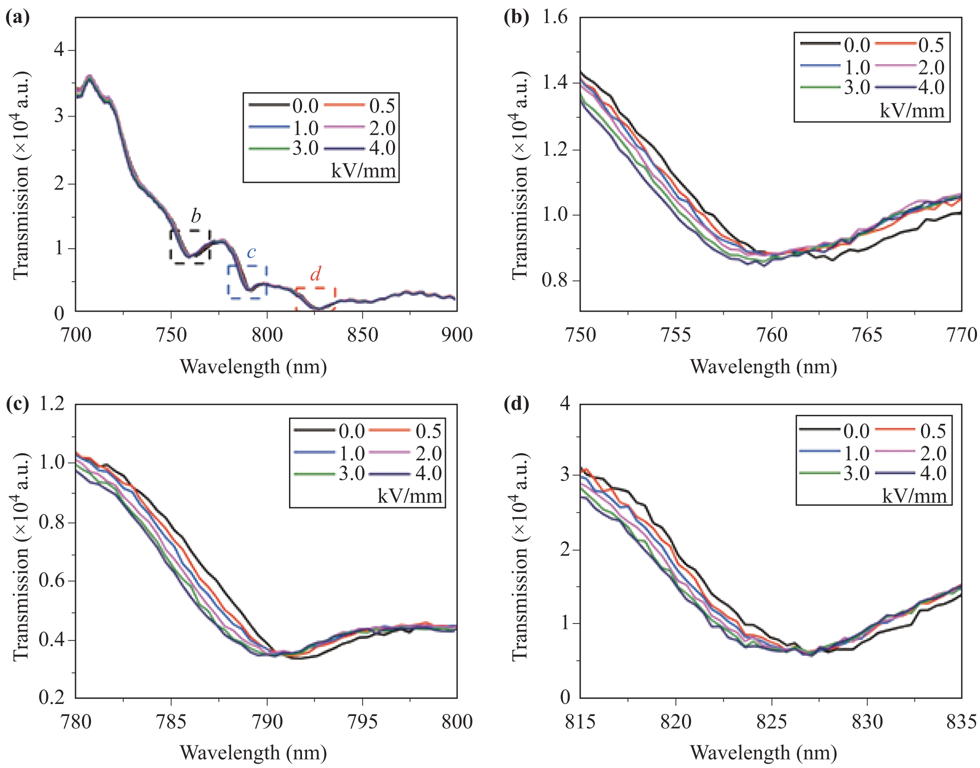

Fig. 2 Transmission spectra of a TiO_2-silicone oil suspension sample in different electric fields. **(b)**, **(c)**, and **(d)** are enlargements of the areas in the dashed boxes in **(a)**. The transmission spectra blueshifted as the external electric field increased. The blueshift was ∼2 nm when the TiO_2 suspension was in a 4.0 kV/mm electric field.

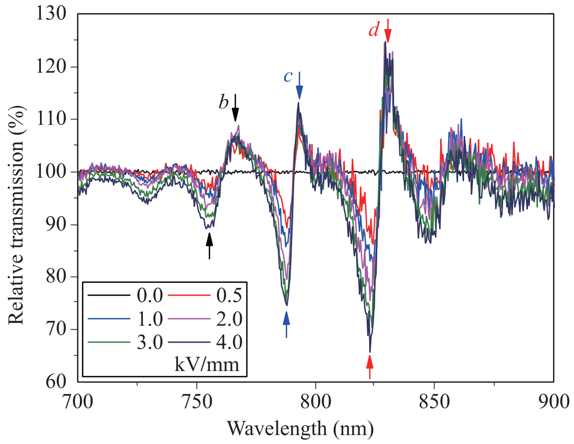

Fig. 3 Relative transmission spectra of a TiO_2-silicone oil suspension sample in different electric fields. The spectra were obtained by scaling the transmission spectra using the same sample in a 0 kV/mm electric field. Each relative transmission spectra exhibits Fano-like asymmetric line shapes. The highest point (lowest point) of each asymmetric line shape increases (decreases) as the electric field increases. b, c, and d indicate the areas that correspond to those in Figs. 2(b), (c), and (d), respectively.

ple in a 0 kV/mm electric field. Interestingly, Fig. 3 shows that the relative transmission spectra have Fano-like [28] asymmetric line shapes. The wavelength range of each asymmetric line shape corresponds to that shown in Fig. 2. Figure 3 indicates that the analogous Fano effect was enhanced as the electric field increased.

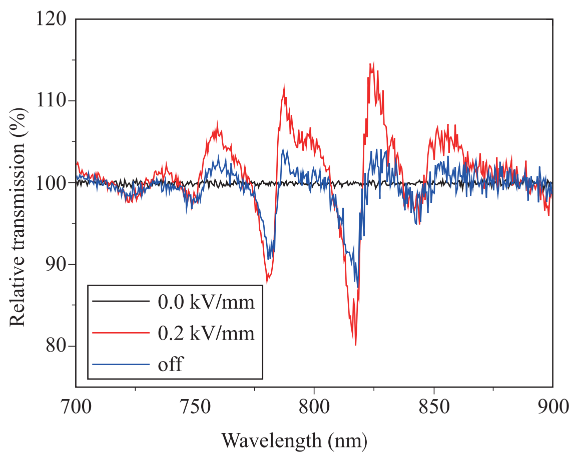

Fig. 4 Relative transmission spectra of a TiO_2-silicone oil suspension sample before an electric field was applied (*black curve*), in a 0.2 kV/mm electric field (*red curve*), and after the electric field was removed (*blue curve*). The analogous Fano effect in the blue curve is weaker than that in the red curve but stronger than that in the black curve. The reference spectrum is the transmission spectrum of the sample in $E = 0$ kV/mm.

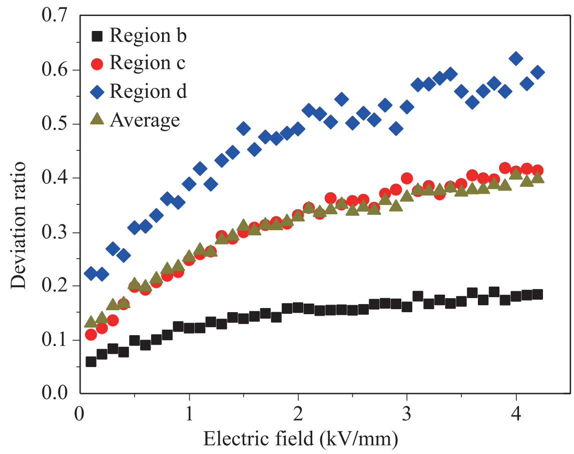

Fig. 5 Relationship between the deviation ratio χ of the analogous Fano effect and the electric field E. Each deviation ratio increases monotonously as the electric field increases.

As the external electric field increases, the TiO_2 particles become more polarized, while simultaneously the disorder of the suspension decreases [30]. Bohren *et al.* [32] showed that the effect of polarization on transmission spectra is very small and can be neglected; the experimental observations presented in Fig. 4 verify this deduction. The transmission spectrum (blue curve) still exhibited Fano-like asymmetric line shapes, even when the electric field was removed. As the depolarization time of a polarized particle is only a few microseconds [33], which is considerably less than the time to record the data, the analogous Fano effect shown by the blue curve in Fig. 4 was caused by the disordered structure of the TiO_2 suspension. The analogous Fano effect of the blue curve is weaker than that of the red curve, which implies that the structure of the TiO_2 suspension is more disordered when there is no electric field. This is consistent with the disordering process caused by the Brownian motion of the TiO_2 particles. Because of the viscous resistance of silicone oil, after the electric field is removed, the stable structure of the TiO_2 suspension should be more ordered than the structure before the electric field is applied [30]. This was also confirmed by comparing the black and blue curves in Fig. 4. Figure 4 shows that the effect of polarization on the transmission spectra was negligible and that the spectral blueshift seen in Fig. 2 was determined mainly by the variation of the disordered structure.

As Bragg scattering increases as diffusive multiple scattering weakens in the structure-ordering process, we conclude that the enhancement of Bragg scattering is the key to the blueshift phenomenon in the transmission spectra. Because the relative transmission spectra in Fig. 3 were derived from the spectra in Fig. 2, the analogous Fano effect is indicative of the interference and competition between diffusive multiple scattering (disordered) and Bragg scattering (periodic).

From Fig. 3, we define the deviation ratio as

$$\chi = \frac{2(T_{\max} - T_{\min})}{T_{\max} + T_{\min}},$$

where $T_{\max}$ and $T_{\min}$ are the highest and lowest transmissions, respectively, in each asymmetric line-shape area. Figure 5 shows χ as a function of E and that it increases as E increases. As the disorder strength of the TiO_2 suspension also decreases monotonously in an increasing electric field, we infer from Fig. 5 that the relationship between χ and disorder strength is monotonous.

3 Conclusion

The structure of a TiO_2-silicone oil suspension changes from a disordered one to an ordered one as the electric field increases. The transmission spectra of a TiO_2-silicone oil suspension exhibited a blueshift during the change, which led to Fano-like asymmetric line shapes in the relative transmission spectra. This analogous Fano effect increased monotonously as the electric field increased. The deviation ratio derived from the analogous Fano effect had a monotonous relationship with the disorder strength.

To understand how the phenomenon of disorder affects the propagation of light, the disorder strength of each sample should be determined [3, 7–10, 19, 21, 22, 26]. This is easily achieved by characterizing the fluctuations in the thickness of the layers in one-dimensional disordered systems [3, 9, 10, 19] and calculating the radial distribution function in two-dimensional disordered systems [26]. However, it is difficult to determine the disorder strength for 3D disordered systems, because the internal structures of the samples are difficult to observe, and therefore, it is not easy to specify the disorder strength of a given 3D sample. However, the monotonous relationship between disorder strength and χ provides a possible method for characterizing the disorder strength of 3D systems where only the spectral blueshift and the analogous Fano effect are required.

Acknowledgements We thank Biqin Dong, Jian Chang, Haiwei Yin, Yafeng Zhang, Yiwen Zhang, Xiangying Shen, Yanwen Tan, and Jian Zi for their fruitful helps and discussions. The financial support of the Science and Technology Commission of Shanghai Municipality (Grant No. 16ZR1445100) is gratefully acknowledged.

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