Time-resolved near infrared spectroscopy for spherical particles as a discontinuous body with isotropic fine structure

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Introduction

In a previous study,[1] we mentioned an application of a non-destructive measurement system newly constructed with a parametric tunable laser to the biological material. Some experiments based on time-resolved spectroscopy were performed by giving attention to the optical characteristics of the cellular structural material like bulk wood. As a result, it became clear that the light propagation in the biological material varied characteristically with the physical construction and the scattering and absorption coefficient of a sample. As the biological material is an inhomogeneous and anisotropic light scattering- and absorbing-medium, it may be difficult to clarify the combined effects of the sample conditions and the wavelengths of the laser beam on the time-resolved profile. So, we intend to explain them by measuring systematically homogeneous and isotropic samples under defined conditions.

In this study, the time-resolved profiles for packed spherical particles of silica were measured precisely to investigate the effect of bulk density and particle size on them. On the basis of such time-resolved spectroscopy, we will estimate the picture of light propagation in a biological material having a complicated cellular structure.

Experimental

Measuring apparatus

The measuring system, which was mainly composed of a parametric tunable laser and a near-infrared photoelectric multiplier, was the same as that used in the previous report.[1]

Samples

The samples used were isotropically packed spherical particles of silica, having a purity of 99.9% (HIPRESICA, UBE-NITTO KASEI Co.). The diameter was 980 ± 20 nm having a coefficient of variation of 2%. Furthermore, another sample, which had diameters ranging from 1100 nm to 2000 nm, was also employed to investigate the effect of particle size dispersion on the time-resolved profile.

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Experiment

The particles were packed into a sample cell made of fused quartz, having an irradiated surface of 10 mm × 40 mm and an apparent light path length of 10 mm. The bulk density varied from 0.49 g cm^{-3} to 0.94 g cm^{-3}. The wavelength of the laser beam was tuned from 450 nm to 1700 nm. The sample cell was inserted into a cell holder having a window with a diameter of 8 mm. The sample, the cooling box containing the near infrared photoelectric multiplier and the optical fibre cable were covered with black cloth to shut off the stray light. The transmitted output power was detected on the opposite side of a sample cell by using a near-infrared photoelectric multiplier through the optical fibre cable. The sampling time and the number for averaging the output power were 100 ns and 300 times, respectively.

Results

Effect of bulk density on time-resolved profile

It is a fundamental problem to clarify the variation of the time-resolved profile with the bulk density of the spherical particles of silica. In this study, the packing condition of the particles was as follows:

(a) Type L: The spherical particles were packed very loosely in a sample cell, so that the spaces between particles were considerably large. The bulk density amounted to 0.49 g cm^{-3}

(b) Type D: The spherical particles were packed densely in a sample cell compared to Type L. The bulk density amounted to 0.64 gcm^{-3}

(c) Type T: In this case, the particles were packed in a sample cell as tight as possible. The bulk density became 0.94 g cm^{-3}.

The time-resolved profiles for these packing conditions of particles having a diameter of 980 ± 20 nm were measured as follows.

Type L

The time-resolved profiles for Type L at each wavelength of the laser beam, λ, are shown in Figure 1(a). Each profile is normalised by the peak value of the transmitted output power to compare the variation of the profile with λ. In this figure, the time-resolved profile without a sample is also illustrated. The time delay of the laser beam caused by passing through the sample, *Ttr*, (the difference between the peak time without a sample and that with a sample) ranges from 1.5 ns to 4 ns. This point will be further discussed in detail. It is also known from this figure that the half width of the time-resolved profile is

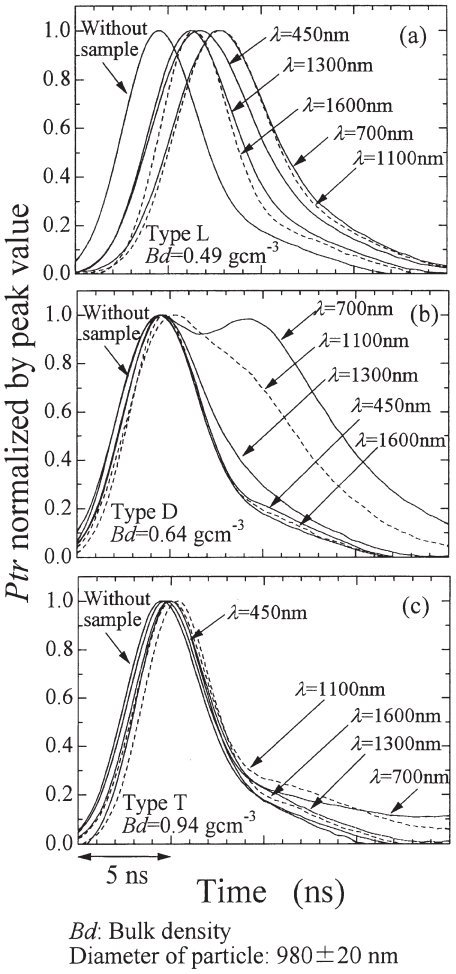

Figure 1. Normalised time-resolved profiles at various packing conditions.

larger than that of the input pulse. Such results suggest that the laser beam is multiply scattered by the bulk of spherical particles of silica.

Type D

The time-resolved profiles for Type D at each λ are shown in Figure 1(b). It is known from this figure that the profile varies extremely with λ. In some specified conditions, we can observe that the time-resolved profile has double peaks although one pulsed laser is used for irradiation. The difference between the first peak and the second one came up to 5.5 ns responding to λ. Not only a bulk density but also some other factors, for example λ or diameter of particle, may be related to such an unexpected result. Later, we will discuss this phenomenon in detail. This way, it was revealed by time-resolved spectroscopy that the laser beam through the clump of spherical particles of silica followed complicated light paths beyond the general knowledge.[2–4]

Type T

The time-resolved profiles for Type T at each λ are shown in Figure 1(c). They are nearly identical to the profile of the input pulse. In this case, the laser beam may follow a straight path regardless of λ.

Characteristic change of light path with bulk density

In this way, it became clear, experimentally, that the bulk density directly governed the circumstance of the time-resolved profile. Next, we will discuss these results coherently.

Figure 2 shows the time-resolved profiles at λ = 700 nm and the models of light propagation at each bulk density. In the case of Type L where the spaces between the particles were considerably large, *Ttr* and the width of output varied with λ so that the laser beam propagated by multiple scattering. Such a feature of the time-resolved profile is analogous to that of a wood sample, where the spaces between the sample material, which are the lumens of the tracheids, have a significant effect.

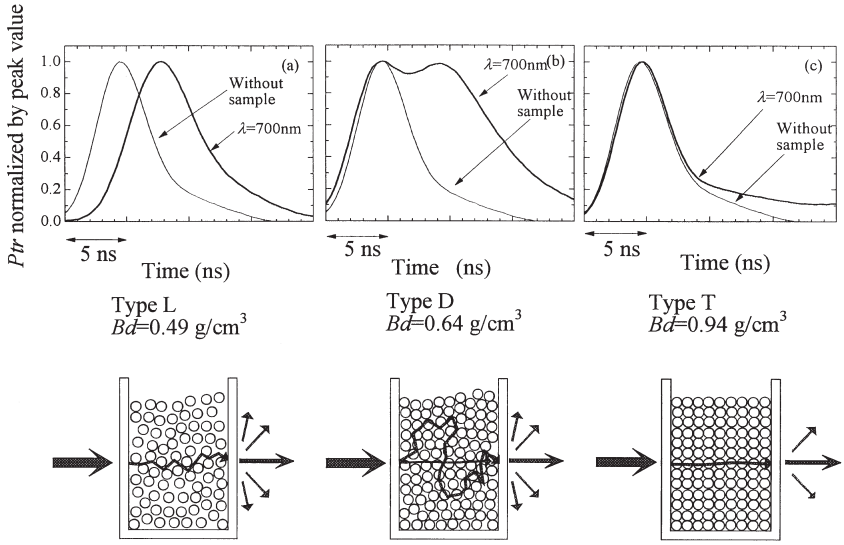

Figure 2. Models of light propagation in sample concerning time-resolved profiles at each bulk density.

In the case of Type D, where the spherical particles were densely but imperfectly packed, we could observe the time-resolved profile having double peaks, although one pulsed laser was irradiated. As shown from this figure, the first peak may reflect the input pulse following nearly a straight light path, in which the complex interactions of light with the particles and the voids are not remarkable. On the other hand, the second peak does mean the existence of multiple scattering of light following complicated paths. In this way, the slight difference in bulk densities yields two contrasting results.

In the case of Type T where the particles were packed in the sample cell as tight as possible, the discontinuities between the particles and the voids have little effect on light propagation, so that the laser beam could follow a nearly straight path.

Effect of combination of wavelength of laser beam and bulk density on time-resolved profile

Here, we will discuss the combined effect of wavelength of the laser beam and the bulk density on the time-resolved profile. The time-resolved profiles at λ = 700 nm and 1400 nm for various bulk densities, *Bd*, are shown in Figure 3. The diameter of the particle is 980 ± 20 nm. It is known from these figures that the time-resolved profile at λ = 700 nm varies characteristically with *Bd*, while that at λ = 1400 nm varies little with *Bd*. To examine such results in detail, the wavelength dependence of the time delay of laser beam caused by passing through the sample, *Ttr*, at each bulk density is illustrated inn Figure 4.

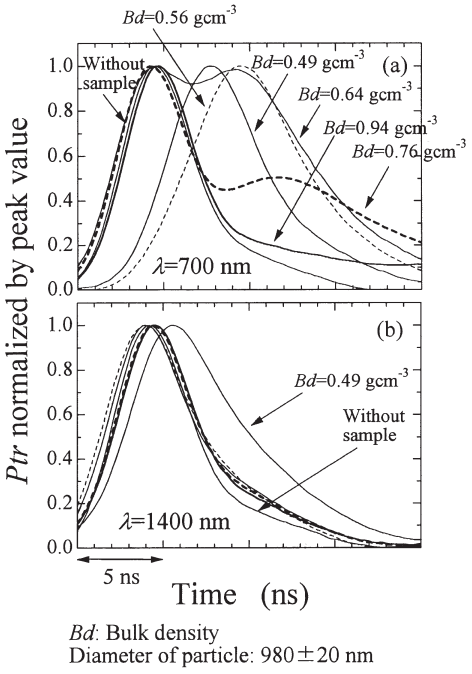

Figure 3. Effect of combination of bulk density and wavelength of laser beam on time-resolved profile.

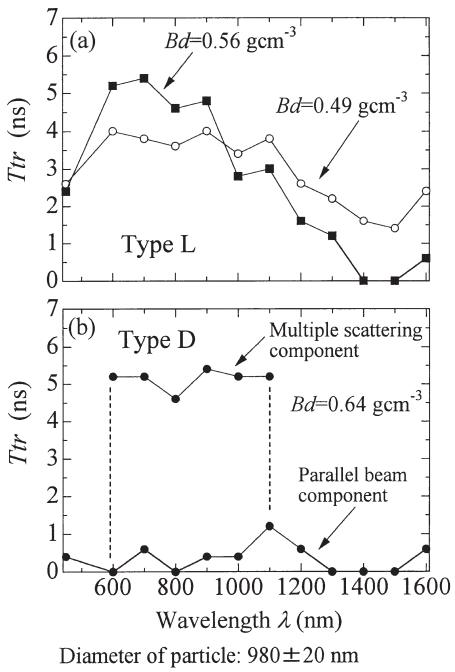

Figure 4. Wavelength dependence of time delay of laser beam passing through sample, *Ttr*, at each bulk density.

In the case of Type L [Bd = 0.49 gcm^{-3} and 0.56 g cm^{-3}; Figure 4(a)], Ttr ranged from 2.5 ns to 5.5 ns at $\lambda < 1100$ nm. Ttr decreased gradually with the increasing λ, then it reached the minimum value at close to λ = 1400 nm. And at Type D [Bd = 0.64 gcm^{-3}; Figure 4(b)], we can observe that the time-resolved profile has double peaks in a limited range of 600 nm to 1100 nm. Ttr at the first peak ranges from 0 to 1 ns and that at the second peak amounts to about 5 ns. In any case, Ttr at λ = 1400 nm amounts to 0 regardless of bulk density, so that the laser beam may follow a nearly straight path. By taking into account that the near infrared spectrum of silica has a major peak at 1380 nm,[5] these observations can be explained by the reduction of multiple scattering due to the absorption.

The refractive index of silica, measured by an immersion method, is 1.39. This suggests that the optical path length of the multiply-scattered component in some peculiar conditions amounts to 100 or more times longer than that of the parallel beam component.

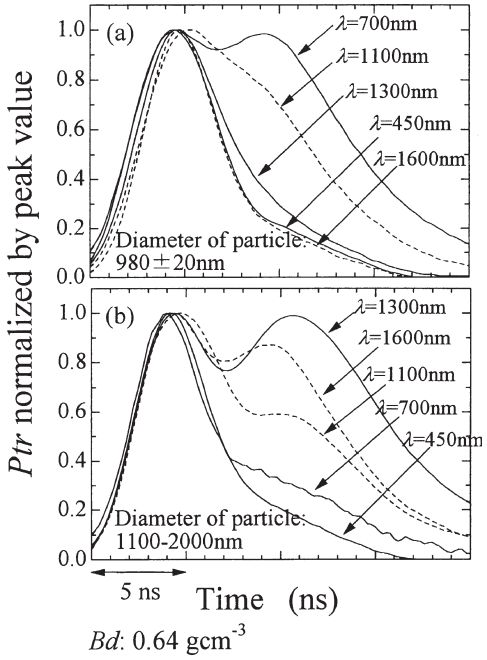

Figure 5. Effects of particle size on time-resolved profiles.

In this way, it was revealed that the time-resolved profile varied drastically with the bulk density and the wavelength of the laser beam relative to the diameter of the particles. The refractive index, the scattering coefficient and the absorption coefficient should also be related to the time-resolved profile. In layers of loosely or densely, but imperfectly packed, particles much of the incident laser beam is multipley scattered under the combined influence of these factors to follow complicated light paths according to our model. And, in layers of tightly packed particles, where the discontinuities between the particles and the voids have little effect on light propagation, the incident laser beam follows a nearly straight path.

Effect of particle size on time-resolved profile

The effects of particle size on the time-resolved profiles are illustrated in Figure 5. The bulk density is 0.64 g cm^{-3} (Type D). We can observe the multiply-scattering component at the extensive range of λ when the particle size is dispersed from 1100 nm to 2000 nm [Figure 5 (b)], while it can be found at the narrow range of λ when the particle size is limited to 980 nm [Figure 5(a)]. The larger the distribution of the diameter of particles, the more complicated the light scattering. The diameter of particles relative to the wavelength of the laser beam must be related to such results. We will discuss this point in the following report.

Conclusion

As the biological material is an inhomogeneous and anisotropic light-scattering and -absorbing medium, it may be difficult to clarify the combined effects of the sample conditions and the wavelengths of the laser beam on the time-resolved profile. To explain them by measuring the homogeneous and isotropic samples under defined conditions, systematically, the time-resolved profiles for the packed spherical particles of silica were measured precisely.

It became clear that the bulk density directly governed the time-resolved profile, for which the refractive index, the scattering coefficient and the absorption coefficient might also be related. Furthermore, they varied characteristically with the diameter of particles relative to the wavelength of the laser beam.

In layers of loosely or densely but imperfectly packed particles, most of the incident laser beam is multiply-scattered under the combined influence of the factors mentioned above. In some specified conditions, we could observe that the time-resolved profile had two peaks, although a pulsed laser was irradiated. The difference between the first peak and the second came up to 5.5 ns responding to λ. The transmitted light of the packed particles must be composed of the parallel beam component and the multiple scattering contribution. Such results suggest that the optical path length of the multiply scattered component in some peculiar conditions amounts to 100 or more times as long as that of the parallel beam component. In layers of tightly packed particles, where the discontinuities between the particles and the voids have little effect on light propagation, the incident laser beam follows a nearly straight path. On the basis of such time-resolved spectroscopy, we shall estimate the picture of light scattering in a biological material having a complicated cellular structure.[6–8]

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