Morphological control and strong light scattering in macroporous TiO$_2$ monoliths prepared via a colloid-derived sol–gel route

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Abstract

Macroporous titania (TiO$_2$) monoliths have been prepared via the sol–gel route started from aqueous anatase-type titania colloid in the presence of poly(ethylene oxide) (PEO), and the light-scattering properties have been investigated by means of coherent backscattering. Well-defined macroporous bicontinuous structures are formed when the transient structure of phase separation is fixed as the permanent morphology by the sol–gel transition. The macroporous morphology, i.e., the size and volume fraction of continuous macropores, can be tailored by adjusting the amount and/or molecular weight of PEO and the TiO$_2$ concentration in the starting solution. During the heat treatment at temperatures above 1000 $^\circ$C, the skeleton is sintered into fully dense body, and the crystalline structure is transformed from anatase to rutile phases, while keeping the macroporous morphology. We show that the rutile-type TiO$_2$-based macroporous monoliths are strongly scattering media for visible light and that the scattering strength can be controlled by the macroporous morphology.

Keywords: Titanium dioxide; Sol–gel method; Phase separation; Macroporous materials; Colloid; Multiple light scattering; Interference of light waves

1. Introduction

It is well established that the propagation of light in dielectrically disordered media (random media) is affected by multiple scattering and interference. Important examples are coherent backscattering (CBS) [1–4] and Anderson localization [5–7]. In order to realize the photon localization in the random media, light must be elastically and extremely strongly scattered. The elastic scattering means that light absorption is negligibly small in the system. The strong scattering is obtained when the wavelength of light is comparable to the size and spatial separation of the randomly distributed scatterers. In addition, the scattering strength increases with an increase in refractive-index contrast.

Pore formation is a very promising technique for tailoring the scattering strength as well as for obtaining strongly scattering media [8–10]. Recently, we have fabricated macroporous monoliths in silica (SiO$_2$)-based sol–gel systems, and investigated the light-scattering properties [11]. The macroporous morphology is formed via the development of a transient structure of phase separation induced by the hydrolysis and polycondensation of alkoxysilane and the subsequent freezing of the structure by the sol–gel transition [12]. The control over the size and density of macropores enabled us to tailor the scattering strength, although the scattering strength was weak because of the low refractive index of SiO$_2$ skeleton ($n$~1.46).

Titanium dioxide (titania, TiO$_2$) with the rutile-type structure is transparent for light in the wide range of the visible spectrum. The absence of light absorption, along with its high refractive index ($n$~2.7), makes rutile-type TiO$_2$ a fascinating material for photonic applications in the visible regions. In spite of this advantage, few works have been performed on porous TiO$_2$. One reason for this fact is the difficulty in preparing porous TiO$_2$ monoliths; in the sol–gel systems derived from titanium alkoxides, it is usually difficult to control the structural development in
the course of the hydrolysis and polycondensation because of the rapid polymerization reaction. Only recently, a first study on the scattering strength of TiO$_2$ monoliths with macroporous bicontinuous morphology was reported, where the strong scattering of visible light was demonstrated [13]. The successful fabrication of porous TiO$_2$ monoliths is achieved by the use of aqueous titania colloid instead of highly reactive titanium alkoxide [14,15]. The pH increase due to the hydrolysis of formamide allows us to control the aggregation and gelation of titania colloid, and an addition of poly(ethylene oxide) (PEO) to the reaction mixture induces the phase separation in the system. The macroporous morphology derived from the sol–gel process accompanied by phase separation can be precisely controlled by the composition and reaction temperature of the starting solution. Our previous study [13] showed that the pore size and porosity of macroporous TiO$_2$ monoliths can be controlled by adjusting the TiO$_2$ concentration and/or the reaction temperature, and that the scattering strength can be altered by the morphological control. The amount and molecular weight of PEO also have significant influences on the macroporous morphology since their parameters alter the timing of the onset of phase separation relative to the sol–gel transition [14,15]. Here, we have prepared rutile-type TiO$_2$ monoliths with a variety of macroporous bicontinuous structures by adjusting the starting compositions and examined their scattering properties. In particular, the relationship between the resultant macroporous morphology and the scattering strength is discussed.

2. Experimental

2.1. Sample preparation and characterization

Aqueous dispersion of titania colloid was employed as the titania source (STS-010, pH = 1.7, Ishihara Sangyo Kaisha, Ltd., Japan). The colloidal particles had the anatase-type structure, and the primary particle size was about 7 nm. PEO [HO-(CH$_2$-CH$_2$-O)$_n$H] having viscosity-average molecular weights ($M_v$) of 100,000 and 300,000 (Aldrich Chemical Co., Inc., Milwaukee, WI, USA) were used as the polymer component to induce the phase separation. Formamide and 1 M aqueous solution of nitric acid (HNO$_3$) (Hayashi Pure Chemical Ind., Japan) were utilized as the solvents to control the gelation and aggregation of titania colloid. The calculated starting compositions and their notations are listed in Table 1.

Table 1
The calculated starting compositions and notations of samples

| Sample      | TiO$_2$ (g) | PEO ($M_v$) | Formamide | HNO$_3$ | H$_2$O |
|-------------|-------------|-------------|------------|--------|--------|
| P300-T215   | 1.98        | 0.0300 (300,000) | 1.16       | 0.177  | 5.84   | 21.5   |
| P325-T215   | 1.98        | 0.0325 (300,000) | 1.16       | 0.177  | 5.84   | 21.5   |
| P350-T215   | 1.98        | 0.0350 (300,000) | 1.16       | 0.177  | 5.84   | 21.5   |
| P375-T215   | 1.98        | 0.0375 (300,000) | 1.16       | 0.177  | 5.84   | 21.5   |
| P300-T154   | 1.98        | 0.0300 (300,000) | 1.16       | 0.322  | 8.96   | 15.4   |
| P325-T154   | 1.98        | 0.0325 (300,000) | 1.16       | 0.322  | 8.96   | 15.4   |
| P350-T154   | 1.98        | 0.0350 (300,000) | 1.16       | 0.322  | 8.96   | 15.4   |
| P1000-T110  | 1.98        | 0.1000 (100,000) | 1.16       | 0.479  | 14.17  | 11.0   |

$^a$The amount of titania in aqueous colloidal titania.
$^b$The sum of the amount of nitric acid in aqueous colloidal titania and that added separately in the process of gel preparation.
$^c$The sum of the amount of water in aqueous colloidal titania and that added separately in the process of gel preparation.

2.2. Light-scattering measurements

For the purpose of evaluating the scattering strength of samples, CBS experiments were performed so that the
transport mean free path of the light, corresponding to the average length after which the propagation direction of the light was randomized by scattering, could be obtained. A collimated beam of the 488-nm line from an Ar\(^+\) laser was reflected by a beam splitter and incident on the sample surface with a small angle from the normal incidence. The sample was rotated around an axis normal to the sample surface in order to average out speckles. The scattered light around the backscattered direction was collected by a lens with a focal point of 5 cm and detected using a charge-coupled device (CCD) placed at the focal point. The transport mean free path was calculated from the dependence of backscattered intensity on the scattering angle [4].

3. Results

3.1. Characterization of macroporous and mesoporous structures

Fig. 1 shows the micrometer-range morphology for dried TiO\(_2\) gels prepared from 21.5 wt\% TiO\(_2\) concentration and varied PEO contents. Figs. 1(a)–(d) represent SEM images of P300-T215, P325-T215, P350-T215, and P375-T215 samples, respectively. All the gel samples exhibit typical macroporous bicontinuous structures, and the sizes of skeleton and macropores increase with increasing the PEO content in the starting mixture. A similar result was observed for gels prepared from 15.5 wt\% TiO\(_2\) concentration and varied PEO content.

We have also inspected the variation in gel morphology with heat treatment. A typical result is shown for P325-T154 sample in Fig. 2. Figs. 2(a) and (b) correspond to FE-SEM images depicting the micrometer-range morphology before and after heat treatment at 1000 °C for 1 h, respectively. One can see that the heat-treated sample retains the macroporous bicontinuous morphology, although overall shrinkage is observed. Figs. 2(c) and (d) represent the higher-magnification FE-SEM photographs taken for the fracture surfaces of TiO\(_2\) skeletons in Figs. 2(a) and (b), respectively. The dried gel is composed of the aggregate of nanoparticles, while the application of heat treatment at 1000 °C brings about the growth of particle size accompanied by the sintering of TiO\(_2\) skeleton. We also confirmed that the macroporous bicontinuous structure is maintained even after the heat treatment at 1200 °C.

Fig. 3 shows the pore size distribution in the micrometer range determined by the mercury intrusion method for samples heat-treated at 1200 °C for 1 h. All the samples possess sharp pore size distributions, which are characteristic of spinodal decomposition. For samples prepared from a fixed TiO\(_2\) concentration (21.5 or 15.4 wt\% TiO\(_2\)) and varied PEO contents, the minor change in PEO content affects strongly the macroporous bicontinuous morphology; the increase in PEO content leads to the increases in both the size and volume of macropores. The pore volume depends more significantly on the TiO\(_2\) concentration in starting compositions. It is clear that the sample prepared from the lower TiO\(_2\) concentration tends to yield the larger pore volume.
As shown in Figs. 2(c) and (d), the nanometer-range structure of TiO$_2$ skeleton is considerably affected by the heat treatment. For the purpose of exploring the effect of heat treatment on the nanometer-range structure in more detail, we carried out nitrogen adsorption measurements so that the pore size distribution in the mesopore regime could be determined. A representative result is shown for P300-T215 sample in Fig. 4. The pore size distributions were obtained from the adsorption branch of the isotherm by the Barret–Joyer-Harenda (BJH) method. The mesopore volume decreases gradually at elevated temperatures, and finally vanishes at 1000°C. In other words, the mesopores collapse almost completely during the heat treatment at 1000°C, indicating that TiO$_2$ skeleton is sintered into the fully dense body. This result is consistent with the morphology change as observed in Figs. 2(c) and (d). As we reported earlier [13], heating at temperatures above 900°C also causes the complete transformation of the crystalline structure of TiO$_2$ skeleton from anatase into rutile phases. Thus, rutile-type TiO$_2$ monoliths with fully sintered skeleton and well-defined continuous macropores can be fabricated via the sol–gel process incorporating phase separation and the subsequent heat treatment.

3.2. CBS

Light-scattering properties have been characterized by CBS measurements. CBS is observed as an increase in the reflected intensity from a medium at the exact backscattering direction as a consequence of the interference of waves propagating along time-reversed optical paths [1–4].
The CBS yields a cone in the plot of the backscattered intensity versus the scattering angle, and the full-width of half-maximum of the cone is inversely proportional to the transport mean free path $l$ [4]. Here, we chose three samples with almost the same pore size but different porosities based on the data of Fig. 3 and compare their scattering properties. Fig. 5 shows the CBS results for the selected samples, i.e., P300-T215, P300-T154, and P1000-T110 samples. The measurements were performed at the wavelength of 488 nm for the samples heat-treated at 1200 °C for 1 h. Also in the figure is shown the CBS result for a macroporous SiO$_2$ monolith prepared via the sol–gel process accompanied by the phase separation [11], for comparison. We obtained $l$ from the fit of diffusion theory [4] to the CBS data, as indicated by solid curves in Fig. 5. For the SiO$_2$ sample, $l = 2.9$ μm, whereas the broader CBS cones for TiO$_2$ samples manifest smaller $l$ values; $l = 1.4$ μm for P300-T215 sample, $l = 1.1$ μm for P300-T154 sample, and $l = 0.66$ μm for P1000-T110 sample. The obtained $l$ values are summarized in Table 2, along with the average pore size and porosity evaluated by the mercury porosimetry. The comparison among three TiO$_2$ samples reveals that when the pore size remains approximately constant, $l$ becomes shorter with increasing the porosity.

### Table 2

| Sample          | Pore size (μm) | Porosity (%) | $l$ (μm) |
|-----------------|----------------|-------------|---------|
| P300-T2.15      | 0.67           | 37          | 1.4     |
| P300-T154       | 0.87           | 49          | 1.1     |
| P1000-T110      | 0.76           | 68          | 0.66    |
| SiO$_2$         | 0.70           | 70          | 2.9     |

*$\phi$ is calculated using the cumulative pore volume and the density of rutile-type TiO$_2$ crystal (4.24 g cm$^{-3}$) (see Ref. [23]) or SiO$_2$ glass (2.2 g cm$^{-3}$) (see Ref. [24]).

4. Discussion

4.1. Macropore formation and morphology control

The electrostatic repulsion among charged particles depends on the pH of reaction solutions. This is because the surface of particles is positively charged at lower pH than the isoelectric point, while it is negatively charged at higher pH. Formamide is hydrolyzed to produce ammonia and formic acid in the presence of strong acid, and the resultant ammonia raises the solution pH gradually. As the solution pH approaches the isoelectric point of titania (pH ~ 5) [16], the electrostatics repulsion is decreased to induce the gelation, that is, the aggregation of titania colloid through van der Waals attraction. Thus, the addition to formamide to the starting solution enables us to control the structural development until the structure freezing due to sol–gel transition.

The fact that the dried gels (without heat treatment) possess macroporous bicontinuous structures as displayed in Fig. 1 indicates that the formation of phase-separated structures is completed at the stage of wet gels. In the present systems containing PEO, the phase separation,
presumably due to spinodal decomposition, is driven by the reduction of an affinity between solvents and PEO adsorbed on TiO$_2$ particles. Hence, initially homogeneous solution separates into two phases; one is rich in the solvent mixtures (solvent phase) and the other rich in the PEO-adsorbed titania phase (gel phase) [14]. Bicontinuous structure, in which both the separated phases are continuous and highly interconnected, can be obtained when the phase separation and sol–gel transition concur to fix the transient structure of phase separation. On drying, the gel phase becomes TiO$_2$ skeleton, and the solvent phase turns into macropores.

Using the aforementioned morphology-formation principle, TiO$_2$ monoliths can be designed with a variety of macroporous bicontinuous structures as demonstrated in Fig. 3. The size of macropores is determined by the timing of the onset of phase separation relative to the sol–gel transition, because a coarsening process is involved in the formation of phase-separated structure in the course of phase separation. The earlier onset of phase separation relative to the sol–gel transition gives rise to more coarsened bicontinuous structures, that is, larger pore size. Our previous studies [14,15] revealed that the addition of a small amount of PEO to the starting solution enhances the phase separation, whereas the excess incorporation suppresses the phase separation. Namely, the phase-separation tendency shows a maximum against the PEO content. Since the PEO contents used here are lower than the PEO content of the maximum phase-separation tendency, the increment in PEO content facilitates the phase separation. Thus, the fact that the pore size increases with the increase in the PEO content (see Fig. 1 as well as Fig. 3) is due to the enhanced phase separation, by which the bicontinuous structure is more coarsened. The phase-separation tendency also depends on the molecular weight of PEO in the starting solution [15]. The lower molecular weight of PEO reduces the phase-separation tendency due to the instability of PEO adsorbed on the gel phase, so the addition of a larger amount of PEO to starting composition is required to prepare gels with bicontinuous structure, as in the case of P1000-T110 sample. By adjusting the content and/or molecular weight of PEO, one can obtain the samples with macropores below 1 μm in size, irrespective of the TiO$_2$ concentration in the starting solution.

On the other hand, the volume fraction of macropores, i.e., porosity, is mainly determined by the solvent fraction in the starting solution, because the solvent-rich phase induced by phase separation changes into macropores after drying. It is apparent from Fig. 3 that the low concentration of TiO$_2$ in starting solution, which corresponds to the high concentration of solvent mixtures, results in the increased pore volume. It is clear that P1000-T110 prepared from the low TiO$_2$ concentration (11.1 wt%) exhibits the large pore volume (~0.45 cm$^3$ g$^{-1}$). The porosity of P1000-T110 is as high as about 68% (see Table 2). Fig. 3 also indicates that the pore volume varies depending on the PEO content, even if the TiO$_2$ concentration is fixed in the starting mixture. We propose two possibilities responsible for the dependence of pore volume on PEO content. A possibility is related to the development of phase-separated structures by spinodal decomposition. The formation process of phase-separated structures by spinodal decomposition can be classified into successive three stages [17]. In the initial stage, concentration fluctuation with a constant wavelength grows only in amplitude exponentially with time. In the following intermediate stage, both the wavelength and amplitude of concentration fluctuation start to increase. Finally, the amplitude of concentration fluctuation becomes constant, whereas the fluctuation wavelength continues to increase so that the interfacial energy is decreased (late stage). The increase in the fluctuation amplitude, which occurs in the two latter stages, corresponds to the coarsening of phase-separated structures. Since the phase equilibrium is established in the late stage, the volume fractions of the separated phases are kept constant during the coarsening process. In the intermediate stage, however, the volume fractions of the separated phases change in the course of coarsening until the phase equilibrium is achieved. If the sol–gel transition in the present systems takes place in the intermediate stage, the gel phase and the solvent phase that turns into macropores after drying will vary both in size and volume fraction depending on the timing of structure-freezing. Another possibility is the difference in the degree of the shrinkage of gel skeleton during the freeze-drying process, which is anticipated for the present PEO-incorporated systems. The PEO entangled on colloidal particles increases the viscosity of gel skeleton and can mechanically support its morphology. As a result, the gel prepared with a large amount of PEO could withstand the stress generated by the shrinkage of skeleton during drying, with continuous macropores being left behind in larger volume. Further experiments are required to clarify these speculations.

### 4.2. Light scattering properties

The scattering strength is defined by the transport mean free path $l$. The small value of $l$ means strong scattering. The transport mean free path is given by

$$l = \frac{1}{\rho \sigma},$$

where $\rho$ is the density of scatterers, and $\sigma$ is the transport cross section [18]. The density of scatterers is calculated as $\rho = f/V$, where $f$ is the volume fraction of scatterers, and $V$ the volume of the scatterer. On the other hand, $\sigma$ depends strongly on a size parameter, defined as the size of scatterers relative to the wavelength of an incident light, $\lambda$, and also increases with an increase in the refractive-index contrast [19]. Under independent scattering approximation where only the scattering characteristics of a single scatterer are involved, $\sigma$ can be calculated for a spherical or cylindrical scatterer according to the Mie scattering
monoliths. Table 2 also indicates that overall results suggest that macropores work as scatterers in the present case. Namely, the sample-to-sample variation of qualitative description based on Eq. (1) is possible in the enough compared to approximation is valid when the size of scatterers is small. The smaller $l/a$ decreases steeply, experiences a minimum, and turns to increases linearly. Kawato et al. [20] measured $l$ over a wide wavelength range for commercially available macroporous SiO$_2$ glasses with different pore sizes but with almost the same porosity and investigated the dependence of $l$ on size parameter $a/\lambda$. They found that $l$ as a function of $a/\lambda$ exhibits a crossover from Rayleigh scattering regime to the regime of geometric optics. A similar trend was observed for macroporous SiO$_2$ glasses prepared via the sol–gel route accompanied by phase separation [11]. These results suggest that the well-defined macroporous monoliths can be regarded as well-characterized random media. However, the use of $a$ obtained from the independent scattering approximation is valid when the size of scatterers is small enough compared to $\lambda$, i.e., the Rayleigh limit ($a/\lambda < 1$), or when the concentration of scatterers is rather dilute. In the case of media with densely distributed scatterers such as our samples, when the size of scatterers is increased to the length scale comparable to or larger than $\lambda$, individual scattering becomes so strong that dependent scattering, i.e., the interaction among scatterers, cannot be ignored. In addition, the bicontinuous structure in our samples may hamper the description that spherical or cylindrical scatterers are randomly distributed. Although improved scattering approximation is required to deduce the more accurate magnitude of $a$ for macroporous media, a qualitative description based on Eq. (1) is possible in the present case. Namely, the sample-to-sample variation of $l$ for macroporous TiO$_2$ monoliths as shown in Table 2 is simply explainable in terms of the pore size and porosity. Among three macroporous TiO$_2$ samples as listed in Table 2, there is not much difference in the size of macropores as well as in the refractive-index contrast, so the sample-to-sample variation of $a$ at a given wavelength ($\lambda = 488$ nm) is assumed to be negligibly small. Under the nearly constant pore size, the higher porosity brings about the smaller separation between pores and in turn yields the higher $\rho$, which is responsible for the smaller $l$. As a result, the $l$ of P1000-T110 sample with high porosity is close to $\lambda/2$ ($\approx 488$ nm), indicating the strong light scattering. The overall results suggest that macropores work as scatterers in TiO$_2$ monoliths. Table 2 also indicates that $l$ decreases by a factor of about 4 for P1000-T110 sample with respect to the SiO$_2$ sample, in spite of the similar pore size and porosity. The smaller $l$ is attributable to larger $\rho$ due to the higher refractive-index contrast between TiO$_2$ skeleton and pores.

In the present investigation, we have focused on how $l$ depends on porosity under a nearly constant size parameter in order to define the kind of scattering centers. Further investigation should be carried out on the dependence of $l$ against the size parameter, because the strong light scattering of macroporous TiO$_2$ monoliths may highlight the interference effect of multiply scattered waves. Such investigation requires the control over the wide range of size parameter, and will be feasible if the pore size can be controlled without changing the porosity or if the wavelength of incident light is varied over the wide ranges. On the other hand, the optical and scattering properties of macroporous TiO$_2$ monoliths open the way to various photonic applications. If emission sources, such as organic dye and semiconductor nanoparticles, are combined with the strong scattering, stimulated emission may be induced by the spontaneous feedback of emitted photons through the interference of multiply scattered light, resulting in mirrorless laser action, a so-called random laser [21]. Also, highly interconnected macropores are suitable for the uniform infiltration of solvents, which provides another opportunity of tuning the scattering strength. An intriguing application which makes full use of the interconnected macropores is a temperature-tunable random laser, which would be readily realized by infiltrating dye-dissolved liquid crystal into the macropores [22]. The present fabrication method offers a unique stage for the external control of the scattering strength, which is a key technology for various applications.

5. Conclusions

We have fabricated macroporous, rutile-type TiO$_2$ monoliths via the sol–gel route started from aqueous dispersion of anatase-type TiO$_2$ colloid in the presence of PEO and demonstrated the strong light scattering of visible light. Monolithic TiO$_2$ gels with well-defined macropores and mesostructured skeleton are obtained by inducing the phase separation parallel to the sol–gel transition. Control over a wide range of the size and porosity of macropores is achieved by adjusting the compositional parameters in the starting solution, including the amount and/or molecular weight of PEO and the TiO$_2$ concentration. While the macroporous morphology is maintained during heat treatment at 1200 °C, the skeleton structure is significantly affected by the heat treatment; the application of heat treatment leads to the grain growth of TiO$_2$ nanoparticles accompanied by the collapse of mesopores and also to the conversion of crystalline structure into the rutile phase whose refractive index is higher than that of the anatase phase. CBS experiments reveal that the transport mean free path $l$ for macroporous, rutile-type TiO$_2$ monoliths is shorter than that for macroporous SiO$_2$ monolith, indicating that the macroporous TiO$_2$ monoliths are more strongly scattering media. The $l$ varies depending on the macroporous morphology; when the pore size remains nearly constant, $l$ is shorter as the porosity is larger. The TiO$_2$ monolith with submicrometer-sized pores (0.76 μm) and high porosity (~70%) is the strongest-scattering medium of visible light among the present samples, with $l$ being close to the wavelength of light ($\approx 0.66$ mm at $\lambda = 488$ nm).
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References

[1] Y. Kuga, A. Ishimaru, J. Opt. Soc. Am. A 1 (1984) 831.
[2] M.P. van Albada, A. Lagendijk, Phys. Rev. Lett. 55 (1985) 2692.
[3] P. Wolf, G. Maret, Phys. Rev. Lett. 55 (1985) 2696.
[4] E. Akkermans, P. Wolf, R. Maynard, Phys. Rev. Lett. 56 (1986) 1471.
[5] P.W. Anderson, Phys. Rev. 109 (1958) 1492.
[6] S. John, Phys. Rev. Lett. 53 (1984) 2169.
[7] D.S. Wiersma, P. Bartolini, A. Lagendijk, R. Righini, Nature 390 (1997) 671.
[8] F.J.P. Schuurmans, D. Vanmaekelbergh, J. van de Lagemaat, A. Lagendijk, Science 284 (1999) 141.
[9] F.J.P. Schuurmans, M. Megens, D. Vanmaekelbergh, A. Lagendijk, Phys. Rev. Lett. 83 (1999) 2183.
[10] J.G. Rivas, A. Lagendijk, R.W. Tkaczyk, D. Vanmaekelbergh, J.J. Kelly, Appl. Phys. Lett. 80 (2002) 4498.
[11] S. Murai, K. Fujita, K. Nakanoishi, K. Hirao, Jpn. J. Appl. Phys.—1 43 (2004) 5359.
[12] K. Nakanoishi, J. Porous Mater. 4 (1997) 67.
[13] K. Fujita, J. Konishi, K. Nakanoishi, K. Hirao, Appl. Phys. Lett. 85 (2004) 5595.
[14] J. Konishi, K. Fujita, K. Nakanoishi, K. Hirao, Mater. Res. Soc. Symp. Proc. 788 (2004) 391.
[15] J. Konishi, K. Fujita, K. Nakanoishi, K. Hirao, Chem. Mater. 18 (2006) 864.
[16] N. Kalay, D. Babic, Colloids Surf. 19 (1986) 375.
[17] T. Hashimoto, M. Itakura, H. Hasegawa, J. Chem. Phys 85 (1986) 6118.
[18] A. Ishimaru, Wave Propagation and Scattering in Random Media, Vol. 1, Academic, New York, 1978 (p. 178).
[19] H.C. van de Hulst, Light Scattering by Small Particles, Dover, New York, 1957.
[20] S. Kawato, T. Hattori, T. Takemori, H. Nakatsuka, Phys. Rev. B 58 (1998) 6180.
[21] N.M. Lawandy, R.M. Balachandran, A.S.L. Gomes, E. Sauvain, Nature 368 (1994) 436.
[22] D.S. Wiersma, S. Cavalieri, Nature 414 (2001) 708.
[23] G.V. Samsonov (Ed.), The Oxide Handbook, Plenum, New York, 1973 (p. 34).
[24] N.P. Bansal, R.H. Dremus, Handbook of Glass Properties, Academic, Orlando, 1986 (p. 57).