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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 °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

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Table 1
The calculated starting compositions and notations of samples

Sample	Content (g)					Fraction of TiO_2 (wt%)
	TiO_2[a]	PEO (M_v)	Form-amide	HNO_3[b]	H_2O[c]	
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.

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 [$HO(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_nH$] 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. Gel samples were prepared from 21.5, 15.4, and 11.1 wt% of TiO_2 concentrations. The sample preparation is as follows. First, appropriate amounts of 1 M aqueous nitric acid and PEO were mixed in a glass tube. Then, formamide and aqueous colloidal titania were added under vigorous stirring in an ice bath. After being stirred for 10 min, the resultant homogeneous solution was allowed to gel at 40 °C in a closed condition. The wet gel was aged at the same temperature for 24 h and was subjected to solvent exchange with 2-methyl-2-propanol. The solvent exchange was repeated five times. The wet gel thus obtained was freeze-dried using a vacuum device (VFD-21S, Shinku Device Co., Japan). Some of the dried gels were heat-treated at temperatures between 600 and 1200 °C for 1 h. A scanning electron microscope (SEM, S-2600N, Hitachi Ltd., Japan) and a field-emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL Ltd., Japan) were used to observe the morphology of dried gels or heat-treated gels. The size distribution of micrometer-range pores was measured by a mercury porosimetry (PORESISER-9320, Micromeritics Co., USA), and the pore size distribution in mesopore regime was determined by nitrogen adsorption-deposition measurements (ASAP-2010, Micrometrics Co., USA).

2.2. Light-scattering measurements

For the purpose of evaluating the scattering strength of samples, CBS experiments were performed so that the