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Reconsideration on structural anisotropy of silica hydrogels prepared in magnetic field

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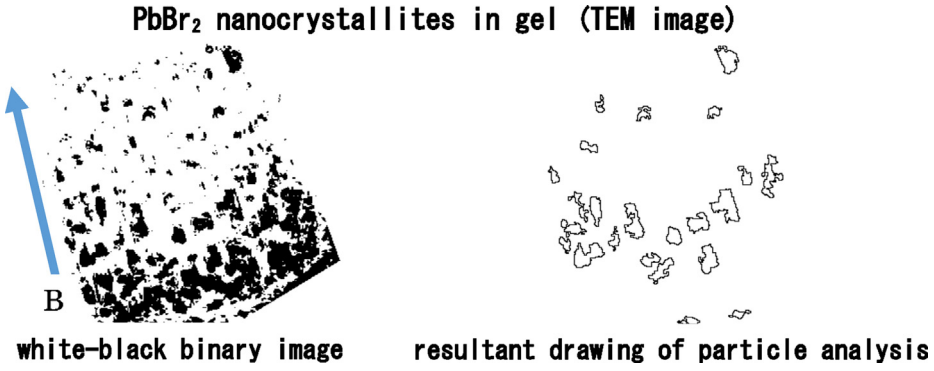
HIGHLIGHTS

- The direction of magnetic alignment of silica gels is reconsidered.
- Results of size/shape of nanocrystallites in gels overturns a previous conclusion.
- Pb(II)-doped silica gel networks aligned along the magnetic field.

GRAPHICAL ABSTRACT



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ABSTRACT

In a previous paper (Mori et al., 2008), we carried out birefringence measurements of Pb(II)-doped silica hydrogels prepared in a magnetic field (***B***). For a 5 T sample, we observed a negative birefringence with the optic axis along ***B***. At that time, providing a positive intrinsic birefringence of silica, we speculated that in the birefringent gels the gel network extended perpendicular to ***B***. The purpose of this paper is to reconsider this speculation on the basis of previous and recent results (Kaito et al., 2006, 2015). In the former, the silica gels were used as a medium of a crystal growth of $PbBr_2$ and aligned arrays of crystallites with long axis parallel to ***B*** were obtained. In the latter, Pb(II) nanocrystallites were formed in silica xerogels by electron irradiation. Both of the short axis of $PbBr_2$ crystallites and the diameter of Pb(II) crystallites were a few tens of nanometers. This size must be a size of short axis of pores in the gel networks elongated affected by the magnetic field. Since the $PbBr_2$ crystallites were elongated along the magnetic field, we conclude that the Pb(II)-doped silica gel networks aligned along the magnetic field.
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1. Introduction

We grew $PbBr_2$ crystals using silica hydrogels prepared in a magnetic field of $B = 5$ T as media of crystal growths [1,2]. Aligned arrays of nanocrystallites are found in gels [1]. The magnetic field was applied during the preparation of the gels and the crystallographic axes of the crystallites were oriented along the direction of

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the magnetic field. Even if a magnetic field was applied during the crystal growth, it did not affect appreciably. Thus, it is anticipated that the magnetic field brought a structural anisotropy in the Pb(II)-doped silica hydrogels during the preparation. Identification of structural anisotropy has, so far, been one of our recent subjects.

There are a lot of potential uses of the silica gels with controlled structure. Therefore, control of the structure of silica gels has, so far, been studied. The transport of materials in the gels depends on the structure. Aerogels can be used as media in column chromatography. If pore size is highly controlled uniformly, the filtering of the column must be improved. One can intuitively realize anisotropy in mechanical and/or thermomechanical properties due to the anisotropic structure. As described in a monograph [3] and reported in literatures such as Refs. [4–8], one can control the structure of silica gels by the selection of starting materials, pH control of the solvent, solvent exchange during polymerization stage, and aging. In addition, porosity of commercially available silica gels for column chromatography was modified by several method [9–13].

Magnetic field applied during the gelation affects the network structure of polymer gels. Chemically cross-linked poly(*N*-isopropylacrylamid) forms aligned network structure perpendicular to the magnetic field [14]. Physically cross-linked agarose gels also exhibit the perpendicular alignment [15]. If side-chain groups prefer the parallel alignment, main chains align perpendicularly. On the other hand, in a case that a magnetic moment is included in a group of the main chain, the main chains align parallel [16].

Because silica is diamagnetic, one cannot imagine the alignment of silica polymers due to direct interaction with a magnetic field. In a previous paper [17], basically base on the results of birefringence measurement and the discussions on a likely mechanism of interaction with the magnetic field, we reached incorrectly at a conclusion that the silica gel network must extend perpendicular to the magnetic field. A negative birefringence on the order of 10^{-6} for 5 T samples, which was a result from a devised Sènarmont method as described in Ref. [17] (also, see Ref. [18] for corrections of typographical errors in Ref. [17]), was interpreted as follows. There have been an interest in the structure of scale around several tens or a few hundreds of nanometers. Pores of such scale have been reported in silica aerogels [19] and commercial gels for column chromatography [11,20]. Also, along with fractal nature, which were more often reported for silica xerogels (such as in Refs. [4–7]), such scales were observed in silica hydrogels [21,22]. It is natural to imagine the existence of closed loops of the same scale in the hydrogels. Let us remember the presence of Pb^{++} ions and that the skeletons made of silicon and oxygen atoms possess a lot of dangling bonds in hydrogels. We speculate ring currents along close loops due to complexes formed on such skeletons with Pb^{++} ions through a mechanism similar to that of electric conduction of the conjugated polymers [23] and the force tending to direct those rings perpendicular to the magnetic field. In this way, providing a positive intrinsic birefringence of silica, in Ref. [17] we struggled to give an interpretation to the negative birefringence from this speculated structural anisotropy. Narrowing of the pore size distribution, which resulted from the scanning microscopic light scattering (SMILS) [24] performed in Ref. [17], can be understood consistently, too. It should be noted that, irrespective of the direction of magnetic alignment, certain characteristic size distributes narrowly if ordering occurs.

The aim of this paper is to overturn the conclusion of Ref. [17] on the structural anisotropy in silica hydrogels prepared in a high magnetic field. To do so, a consideration is given relying on a previous result [1] and a recent one [27] with help of a result of the reinvestigated birefringence [18]. Further analysis of SMILS result in Ref. [17] is also given.

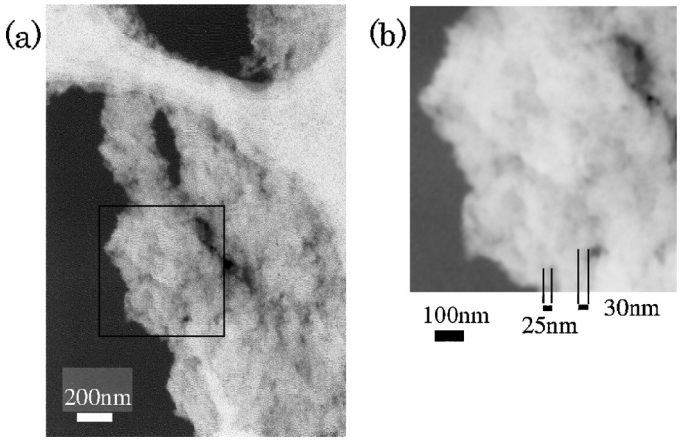

Fig. 1. (a) A TEM image of Pb(II) nanocrystallites formed inside macropores of a silica xerogel prepared in 10 T induced by electron irradiation [27] (this image is not a reuse of one in Ref. [27]), and (b) a magnification of a part of (a), indicated by a square. Sharpness has been reduced to recover the quality of magnified image. Among many crystallites two pairs of vertical lines have been added to two of them for guide for eyes in (b).

2. Materials and methods

In Ref. [17] as well as in Refs. [1,26], the samples were prepared in the same way as described previously [25], except for the application of magnetic field. The starting material was sodium metasilicate, the acid to maintain the solution strongly acidic was acetic acid, and the source of Pb(II) was a $Pb(NO_3)_2$ aqueous solution.

In Ref. [27], unlike previous studies [1,2,17], a lead (II) acetate aqueous solution was employed as the source of Pb(II). After preparing silica hydrogels in a magnetic field of various strengths like in Refs. [1,2,17], the samples were dried in test tubes as prepared for a year. Then, electrons were irradiated to the samples in a transmission electron microscope (TEM) environment. We observed the samples by a TEM (Hitachi H-9000NAR).

We should note on the difference between the mechanisms for crystallization in those two kinds of experiments. In the former, crystallization is governed by the diffusion of Br^- ions and reaction with Pb^{++} ions thereafter. In the latter, such diffusion-reaction mechanism does not exist. Pb^{++} ions are reduced by irradiated electrons and then metallic Pb clusters precipitate.

3. Results and discussion

We have recently reported formation of Pb(II) nanocrystallites induced by electron irradiation inside macropores of Pb(II)-doped silica xerogels prepared in a magnetic field of various strengths [27]. A TEM image is shown in Fig. 1. Nanocrystallites are observed in aggregates inside macropores. A part of Fig. 1(a) is taken up in Fig. 1(b). Sharpness has been reduced and two pairs of vertical lines have been inserted auxiliary. Their sizes are a few tens of nanometers, which coincide to the length of short axis of $PbBr_2$ nanocrystallites in Fig. 3(a) of Ref. [1] [carried into this paper as Fig. 2(a)]. It is noted that due to the reduction of sharpness we failed to put smaller crystallites in relief as indicated. Those sizes must be the length of short axes of pores elongated affected by the magnetic field in the hydrogels. We guess that similar structures remain inside macropores in the xerogels. During drying process of hydrogels, macropores form. Therefore, the microstructure of xerogels also more or less differs from that of hydrogels. Nevertheless, there must remain gel network structure in macropores similar to that of hydrogels. From the fact that the orders are the same, we

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