



An approach for highly transparent titania aerogels preparation

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ABSTRACT

Titania aerogels are synthesized using various solvents for sol preparation. The morphology, the optical transmittance, the phase composition and the specific surface area of samples are determined. The sample prepared from isopropanol is found to be white and light-tight and to consist of fibers about 17 nm wide. The fibers are crystalline and have an anatase structure. The specific surface area of the sample is 150 m²/g. The samples prepared from methoxy- or ethoxyethanol are transparent yellowish monoliths. They are X-ray amorphous and consist of spherical nanoparticles 1.5–3.5 nm. The specific surface area of these samples is more than 500 m²/g. Transparent titania aerogels are prepared in all-solution approach for the first time.

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1. Introduction

Transparent porous oxides have recently attracted deep interest because of their potential wide applications. Among them, transparent silica porous glasses and aerogels have received the most study [1,2]. Other functional porous oxides, including titania, have also attracted considerable attention [1,2]. Porous titania-based devices can be used as photocatalysts [1], electrodes in wet solar cells [3], and various gas sensors [4–6].

Titania aerogels represent one of the most promising classes of porous titania due to unique properties inherent to these materials, namely, a high porosity and a low density. There are several methods for the preparation of transparent titania wet gel and xerogel monoliths [7]. However, there are only a few works on obtaining transparent titania aerogels [8–10]. But the authors used a complex multi-step process for the semi-transparent titania aerogels' preparation. Transparent titania aerogels can be efficiently used as coatings for antifogging mirrors [11], solar cells, and chemical or medical sensors [7].

In this work we have developed a simple method for synthesizing a highly transparent titania aerogel monoliths.

2. Materials and methods

Titanium (IV) isopropoxide (98+%), propylene oxide, (99.5%), isopropanol (99.5+ %), HCl (37%), diethyl ether (99%) 2-methoxyethanol (99.8%), and 2-ethoxyethanol (99%) were used as received (Aldrich). Titania sols were prepared as follows: 0.5 mL HCl (6N) was added to 2.7 mL methoxyethanol, isopropanol or ethoxyethanol, and the mixture was stirred for several minutes until heating stopped. Titanium isopropoxide (0.67 mL, 2.25 mmol) was then added. The reaction mixture was stirred for 2 min and propylene oxide (300 μL) was added in three equal portions under continuous stirring. The formed sols were placed into sealed plastic molds, and allowed to gel. Gelation typically took 3–5 min for alkylglycols and a few seconds for isopropanol. The prepared samples were washed five times *via* soaking in diethyl ether, the solvent was exchanged daily. Then the aerogels were dried under supercritical conditions in CO₂ at 50 °C and 15 MPa.

The specific surface area (SSA) measurement, X-ray diffraction (XRD) analysis and TEM investigations were performed as in [12]. The transmission spectra of transparent aerogels (6 mm thick) were recorded with an Ocean Optics QE65000 UV-VIS spectrometer with a DH 2000 halogen–deuterium light source.

3. Results and discussion

We found that the MeGI and EtGI-samples (synthesized using 2-methoxyethanol, and 2-ethoxyethanol respectively) were

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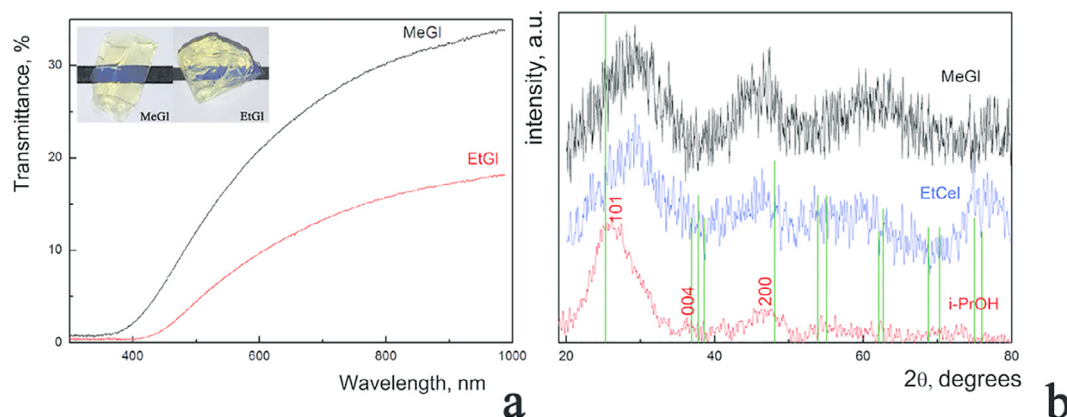


Fig. 1. Optical transmittance of MeGI and EtGI samples (6 mm thick) vs. the wavelength (a) and XRD patterns for i-PrOH, EtGI and MeGI aerogel (b).

transparent yellowish monoliths, while the i-PrOH-sample was white and light-tight. The yellowish color of the transparent aerogels is due to Rayleigh scattering by solid gel network heterogeneities in the nanometer range [13].

The optical transmittance of the samples depends on the wavelength (Figure 1a). The transmittance of aerogels in the near visible region is well described by the Eq. (1):

$$T = A \exp(-Ct/\lambda^4), \quad (1)$$

where T is the transmittance, A is the wavelength-independent coefficient related to scattering from the surface due to the damages and cracks that exceed the light wavelength [14], C is the Rayleigh scattering intensity, t is the sample thickness, and λ is the wavelength. Aerogels with a high value of A and a low value of C should have the maximum transparency. This equation allows us to compare the transparencies of aerogels of various thicknesses, origins, and surface conditions. A and C values estimated from the experimental curves (Fig. 1) are given in Table 1.

Figure 2a, d, g shows the results of TEM investigation of the aerogels. It is clearly seen that the MeGI and EtGI-samples have a similar microstructure: the materials consist of an interconnected network of spherical nanoparticles 1.5–3.5 nm size (Fig. 2a,d). Such type of a microstructure is typical for many metal oxide aerogels [12,15]. These particles are mainly amorphous and contain only a few number of crystallites (Fig. 2b, e). The crystallites are recognized as the anatase phase by the Fast Fourier Transformation (FFT) patterns (Fig. 2c, f). The i-PrOH-sample has a very different morphology. Instead of spherical particles, the microstructure consists of fibers about 17 nm wide (Fig. 2 g). The fibers consist of crystallites with an anatase structure. These crystallites are misoriented and shifted to each other judging by the displacement of the crystal planes. They are of the size about 1.5 nm. The fringes of the atomic planes that are aligned along the fiber axis correspond to the (1 0 1) anatase plane.

The XRDA (Fig. 1b) confirms the TEM data. It is seen that the MeGI and EtGI-samples are amorphous and the i-PrOH sample is

crystalline and has an anatase structure (JCPDS 21-1272) with the grain size of 1.5 nm.

It was found that the MeGI and EtGI-aerogels have a SSA of 517 m²/g and 560 m²/g, respectively, which is significantly larger than that of the i-PrOH-sample (150 m²/g).

We found that in the case of methoxy- or ethoxyethanol, the gelation time increases significantly (3–5 min for glycols and a few seconds for i-PrOH). It is well-known that metal alkoxides are sensitive to water [16,17]. Usually, hydrolysis and condensation reactions with Ti(IV) alkoxides are very fast due to a significant partial positive charge at Ti atom [18]. Thus, we can conclude that the use of glycols leads to the formation of species with enhanced resistance to hydrolysis and condensation.

It is well known that titanium (IV) alkoxides can be subjected to *trans*-esterification in the presence of other alcohols. If methoxy- or ethoxyethanol is used, Ti(IV) chelates are thought to be formed according to the Fig. 3.

The consequence of chelation manifests itself in increased resistance to hydrolysis and condensation.

To eliminate the influence of the alcohol molecule length, we performed gelation in *n*-butanol (possessing the same chain length and having no chelating properties) and obtained a light-tight titania aerogel.

At the present time, we cannot offer a satisfactory explanation of the glycols' influence on the aerogels' transparency. It was found that the microstructure of i-PrOH-samples differs from that of MeGI and EtGI-samples considerably. i-PrOH-samples consist of fibers hundreds of nanometers in length. These formations serve as an effective light scattering centers. In our opinion there are two points which support agglomeration-free gelation avoiding agglomerates scattering the light and thus improving transparency in glycols. Ti(IV) chelates are more stable to hydrolysis, that reduces the speed of gelation and leads to less branching and less bulky structure [8]; and titania nanoparticles (formed in solution) are covered by organic molecules of EtGI or MeGI, that makes the nanoparticles building blocks better dispersed and more agglomeration free.

Thus, we found a facile procedure to prepare transparent titania aerogels. They have a large SSA and X-ray amorphous structure. Although we cannot explain the differences between the i-PrOH and alkyl glycols samples, the main reason of the different properties of the samples is thought to be different interactions of titanium alkoxide with the solvent. In contrast to isopropanol, alkyl glycols can chelate the titanium ion and change the gelation kinetics and gel structure.

Table 1
Optical parameters of titania aerogels.

Sample	A	C (μm ⁴ /cm)
MeGI	0.36	0.124
EtGI	0.2	0.169

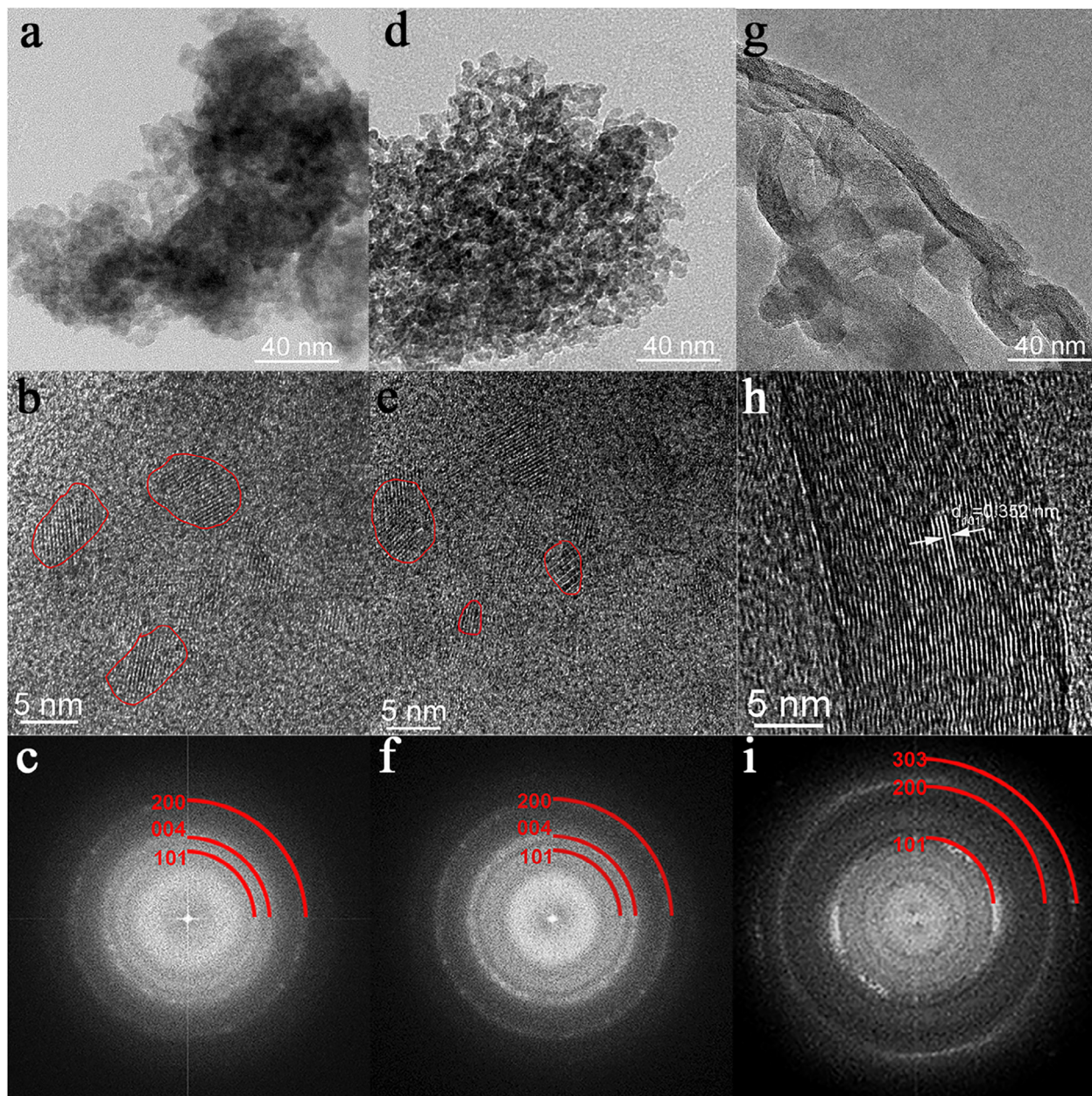


Fig. 2. Bright field TEM, HRTEM, and FFT images of MeGI (a, b, c), EtGI (d, e, f) and i-PrOH (g, h, i) samples.

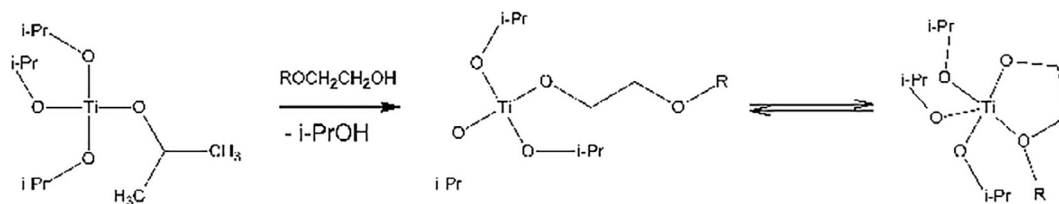


Fig. 3. Scheme of chelation of titanium alkoxide by alkyl glycol.

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