



The effects of hydrolysis level on structural properties of titania aerogels



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ABSTRACT

In this paper seven titania aerogels with different hydrolysis levels from 3.75 to 9 were prepared by sol-gel method and subsequent drying by supercritical CO₂ dynamic extraction at 75 °C and 220 atm. The effects of the amount of water as hydrolysis agent was considered by observing the destruction of the gels during the aging period and investigating the porosity, specific surface area and pore volume of the aerogels. Besides a portion of some of the samples were calcined up to 450 °C to achieve anatase crystalline phase which formation was examined by XRD and Raman spectroscopy measurements. The observations showed that the gels with lower hydrolysis levels (3.75 and 4) were not stable enough and dissolved during the aging period. From the physical stability of the gels and the structural characterizations of the prepared aerogels, an optimum hydrolysis level equal to 7.35 was chosen. The aerogel prepared with this hydrolysis level has a specific surface area of 639 m² g⁻¹, and its anatase phase (after the calcination of the aerogel up to 450 °C) has a specific surface area of 157 m² g⁻¹.

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1. Introduction

Using different methods of synthesis and characterization to create new categories of materials has made nanotechnology one of the most effective branches of science in human lives. Nanotechnology is the ability of controlling the chemical and physical properties of nanostructures through changing their dimension and morphology. Using different methods to synthesize nanostructures enables the production of desired materials for specific applications. One group of these new materials is aerogels that due to their unique properties have been replaced by other nanostructures [1–3].

Aerogels: the three dimensional (3D) interconnected mesoporous solid network with low density, high specific surface area and extremely porous structure, can be made from different materials for specific purposes [4,5]. Sol-gel process controls the structural and chemical properties of the (aero) gel while supercritical drying (SCD) preserves the open gel network during the drying process, [6–9] resulting in the extreme porous structures. Up to 95% of the volume of an aerogel is air [5], leading to remarkable physical-chemical properties, such as low thermal conductivity, low longitudinal sound velocity, small index of refraction and large specific surface area. Among these properties, high specific surface area is a key factor in many applications such as catalysts, sensors, fuel storage, ion exchange, target for ICF and etc. ... [2,10].

Among different wide bandgap semiconductors, TiO₂ is commonly used as a photocatalyst for water splitting, air and water purification and decomposition of organic pollutants due to its conduction and

valence band energies, high photosensitivity, high photostability, strong oxidation power of its holes and redox selectivity [3,11–13]. Furthermore, different structures of TiO₂ as a typical photoanode in Dye Sensitized Solar Cells (DSSCs) have been used to improve the efficiency of this kind of solar cells [14–16]. On the other hand, after being modified with plasmonic nanoparticles such as gold or silver, Au/Ag-TiO₂ composites become one of the best candidates for Surface-Enhanced Raman Spectroscopy (SERS) substrates in sensing applications [1,17,18]. The above-mentioned intrinsic characteristics of titania, accompanied by being nontoxic, environmentally friendly and having low cost make it one of the most popular materials for photovoltaic and photocatalytic activities [19,20].

Despite the mentioned positive features of TiO₂, there are some important drawbacks associated with this oxide, such as: relatively small specific surface area (typical Degussa P25 has a specific surface area: $S_{\text{BET}} = 50 \text{ m}^2 \text{ g}^{-1}$), large bandgap energy around 3–3.2 eV (ultraviolet light) and fast recombination of electron-hole pairs [1,19,21–24]. The photocatalytic activity of TiO₂ is strongly influenced by its morphological parameters such as crystal structure, specific surface area, porosity and surface hydroxyl group density [21]. As the same parameters apply in DSSCs, it becomes necessary to use a photoanode with specific characteristics, such as: (1) high specific surface area to load more light absorbing dyes, (2) high porosity to enable fast and easy mass transfer of dye molecules to the semiconductor and electrolyte ions through the porous structure and (3) 3D interconnected network for charge transportation to lessen the unwanted back electron transfers [16]. To improve these intrinsic weaknesses of TiO₂, different strategies had been used either by narrowing the bandgap or modifying morphology in a systematic way to obtain higher specific surface areas [13,25,26].

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The subject of this paper is TiO₂ aerogel as a developing material, benefiting both from the unique morphology of most common aerogels and intrinsic properties of titania. Different methods of synthesis have been previously reported [20,27–29]. Since producing high specific surface area TiO₂ aerogel improves its various applications, the effect of hydrolysis level as one of the sol-gel controlling parameters on the aerogel morphological properties has been studied. In this paper by examining different methods and hydrolysis levels, a new molar ratio was obtained that seemed to be more appropriate for preparing both a stable gel and obtain a high specific surface area aerogel.

2. Materials and methods

2.1. Synthesis of TiO₂ aerogels

In order to observe the effects of hydrolysis level (*h*; molar ratio of water to metal alkoxide) on the chemical, physical and structural properties of aerogels, several TiO₂ gels were prepared with acid (HNO₃) catalysed sol-gel method using titanium(IV) isopropoxide (TIP) as the precursor. The molar ratio of TIP/ ethanol/acid was kept constant: 1/21/0.08, in all the samples while the ratio of water to TIP (hydrolysis level) was changed from 3.75 to 9 as presented in Table 1. In the sol-gel process of synthesizing the gels, after adding water in the last step, the solution was stirred for a few seconds and then the sol transformed to gel and the magnet was prevented from moving (gel time). The gel time differed from one sample to another according to amount of water introduced to the solution. It seems that the gel time is inversely proportional to the hydrolysis level; it decreases from a few seconds at hydrolysis level 3.75 to instantaneous formation of the gel after adding the last drop of water at hydrolysis levels 8 and 9 (Table 1).

The prepared gels were aged at room temperature in ethanol bath for >40 days. Then, after 3 times solvent exchange with acetone every 24 h, the solvent was extracted supercritically with CO₂ (75 °C, 220 atm).

A portion of some of the dried samples as kept amorphous while the remaining portions were calcined at 450 °C for 2 h. (ramp at 2 °C min⁻¹, hold for 2 h, cool at 2 °C min⁻¹). The amorphous samples are labelled TA-*x* and the calcined ones TA*h*-*x*, where *x* indicates the number of the hydrolysis level.

2.2. Structural characterization

Field emission scanning electron microscope (FESEM) images were collected after the samples were coated with a conductive gold layer with a Tescan MIRA scanning electron microscope with a field emission tip operated at 15 kV.

The specific surface area of the prepared aerogels were determined by the Brunauer-Emmet-Teller (BET) method, in a partial pressure range of 0.05 < *p*/*p*₀ < 0.4 and the N₂ adsorption was carried out at 77 K. The samples were preheated before each measurement at

120 °C. The total pore volume and the type of porosity of the samples were obtained from the N₂ adsorption/desorption isotherms at a partial pressure of 0.99 and the distribution of the pore radii from Barrett-Joyner-Halenda (BJH) method.

The Raman measurements of the TiO₂ aerogels calcined at 450 °C were performed with a Thermo Nicolet Almega dispersive Raman scattering spectrometer operated at 532 nm laser line in a back-scattering configuration.

The X-ray diffraction patterns were obtained by using a Philips X'Pert MPD powder diffractometer, working at 40 kV and 40 mA. The CoKα (λ_{CoKα} = 1.78897 Å) radiation, collected in a step-scanning mode with Δθ = 0.04°/s. The 2θ values have been converted from Co anode to Cu one and the converted XRD patterns are presented.

3. Results and discussion

All the prepared gels were aged in sealed beakers filled to the top with solvent liquid (ethanol) for >40 days. This solvent bath protects the gels from drying during the aging period when different reactions are still in process. In the preparation of inorganic gels, the chemical reactions do not stop even after a continuous network has been formed (after the gel time). There are still condensable particles left in the pore liquid that would slowly agglomerate to the existing network. On the other hand, the gel network is still very flexible and the neighboring Ti-OH or Ti-OR groups can approach each other and condense together. In addition to the condensation reactions, due to Ostwald ripening, small particles condense together and small pores are filled. Aging is the period in which these reactions take place and thus leading to the increase of the stiffness of the gel. This is an important element for reducing the shrinkage and cracking of the gel during the preceding supercritical liquid extraction [5].

After 4 weeks of observing the evolution of the physical appearance of the prepared gels during the aging period, the reduction in the volume of the gels with hydrolysis levels 3.75 and 4 (samples TA-3 & TA-4) hinted at dissolution. These gels were completely transparent, though apparently not stable enough because after 50 to 60 days there was no trace of the gels in the beakers. However, after 70 days, no change was detected in the volume of the samples TA-6 to TA-9. These titania gels were all stable and translucent. The experiment was carried out several times with different synthesis procedures and the same results were obtained. In some cases the gels were dissolved after 2 weeks of aging! It can be surmised that “syneresis” might be the reason of dissolution of the gels. These observations lead to the conclusion that syneresis is an inevitable event in the aging process. However, apparently increasing the hydrolysis level can compensate for the volume reduction due to syneresis. After about 40 days of aging, nothing remained from samples TA-3 and TA-4, and sample TA-5 was not stable enough to be dried. Thus, only samples TA-6, TA-7, TA-8 and TA-9 were supercritically dried and been characterized.

Table 1
Molar ratio and structural characterization of the prepared TiO₂ aerogels and the calcined samples.

TiO ₂ aerogel	Molar ratio TIP/EtOH/HNO ₃ /H ₂ O	Gel time (s) ^a	BET surface area (m ² g ⁻¹) ^b	Total pore volume (cm ³ g ⁻¹) ^b	Ave. pore diameter (nm) ^b
TA-3	1/21/0.08/3.75	30	–	–	–
TA-4	1/21/0.08/4	28	–	–	–
TA-5	1/21/0.08/5	14	–	–	–
TA-6	1/21/0.08/6	9	436	0.52	4.8
TA-7	1/21/0.08/7.35	4	639	2.25	14.1
TA-8	1/21/0.08/8	Instantaneously	617	2.09	13.5
TA-9	1/21/0.08/9	Instantaneously	655	1.50	9.1
TA <i>h</i> -6	1/21/0.08/6	–	102	0.24	9.5
TA <i>h</i> -7	1/21/0.08/7.35	–	157	0.63	16.1
TA <i>h</i> -8	1/21/0.08/8	–	149	0.76	20.4
TA <i>h</i> -9	1/21/0.08/9	–	132	0.49	14.9

^a Calculated from the videos that had been taken during the gel formation.

^b These are the results from BET and BJH measurements.

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