JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 3, March 2007, p. 668 - 671

Evaluating the thermal treatment parameters effect on the anatase nano crystallites size of titania aero gels

L. BAIA[a*], M. BAIA[a], A. PETER[b], V. COSOVEANU[b], V. DANCIU[b]
[a]*Faculty of Physics, Babes-Bolyai University,400084 Cluj-Napoca, Romania*
[b]*Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 400028 Cluj-Napoca, Romania*

A semi-empirical model is applied to investigate a series of TiO_2 aerogels annealed at different temperatures. Specific information concerning the nature of the aerogels networks and correlations between the crystallites size and spectral features of the 144 cm^{-1} Raman band are obtained. Based on these findings the as prepared aerogels were heat-treated at different temperatures (400-700 ˚C) for various time intervals (1-5 h) and investigated in an attempt to optimize this type of nano-architectures for further experiments in which certain sizes of the TiO_2 anatase nanocrystallites are required. The careful analysis of the three dimensional relationship between the crystallites mean size, the temperature and the time of the thermal treatment reveals that the most pronounced effect of these parameters on the anatase crystallites dimension appears for the aerogels annealed at 600 ^{0}C for different times, where the largest spread of the crystallites dimension occurs.

(Received November 15, 2006; accepted December 21, 2006)

Keywords: TiO_2 aerogels, Crystallites mean size, Raman spectroscopy, XRD

1. Introduction

Nanometer-sized materials have recently gained a huge interest due to their distinctive physical and chemical properties and their importance in technological applications [1]. Because of their large surface-to-volume ratios and quantum-size effect, their properties and structural stability are very different from their bulk counterparts [2-5].

Aerogels are a special class of highly porous materials that are being studied for a variety of applications mostly as novel insulator but also as Cherenkov detectors, catalysts and catalysts supports, filter membranes, acoustic delay lines, etc. [6]. Particularly, TiO_2 aerogels and, especially their crystalline phase anatase, are attractive for their applications in solar energy conversion, photocatalysis [7-9].

Having in view that every property, e.g. optical properties, dielectric constant, diffusion mechanism, of semiconducting nano-materials is size dependent [10] the designing of TiO_2 porous nano-architectures formed by anatase nanocrystallites of a few nanometers in diameters, but having controllable mean sizes, close packed into mesoparticles of tens of nanometers represents a real challenge.

Recently, based on a semi-empirical model that was applied to investigate a series of TiO_2 aerogels annealed at different temperatures for two hours we were able to obtain specific information concerning the nature of their network and to find a correlation between the crystallites mean size and the broadening of the Raman band located at small wavenumbers [11]. It should be mentioned that the investigated aerogel had the highest Brunauer-Emmet-Teller (BET) surface area from all prepared aerogels by varying the synthesis parameters. The obtained results made possible the dimensional characterization of the TiO_2 crystallites of this type of aerogel by simple measuring of a Raman spectrum. In the present work, our interest is to obtain and evidence TiO_2 aerogel structures of anatase type, which contains of crystallites that cover a large interval of dimensions, and to extend the investigation area of this special class of materials by applying the above correlation to TiO_2 aerogels heat-treated at different temperatures (400-700˚C) and various time intervals (1-5 h), in an attempt to optimize this type of nano-architectures for further experiments in which TiO_2 nanocrystallites of certain sizes are required depending on the desired functionality.

2. Experimental

Samples preparation

TiO_2 gels were prepared with the acid (HNO_3)-catalyzed sol-gel method by using titanium isopropoxide (TIP), HNO_3, EtOH and H_2O with the 1/0.08/21/3.675 molar ratio. The gels were allowed to age for at least 40 days. Before drying, the gels were successively washed with excess of fresh alcohol, at least four times and were kept in alcohol from a week to several months. The as prepared TiO_2 aerogels were subjected to a thermal treatment at 400, 450, 475, 500, 550 and 600 ^{o}C for 2h. The samples were also separately heat-treated at 400, 500, 600 and 700 ^{o}C for 1, 2, 3, 4 and 5 hours.

Samples measurements

For the SEM measurements a piece of aerogel sample was mounted using conductive graphite paint on aluminum stubs than coated with a conductive gold layer. Before coating with gold the sample was kept for one hour at 150^0 C to remove any moisture. The SEM images were collected with a JEOL 7601F electronic microscope with a field emission tip that operated at 10 kV.

A radiation of 1064 nm from a Nd-YAG laser was employed for the recording of the Raman spectra of the untreated and heat-treated TiO_2 aerogels. The FT-Raman spectra were recorded using a Bruker Equinox 55 spectrometer with an integrated FRA 106 Raman module, a power of 100 mW incident on sample and a resolution of 1 cm^{-1}.

The X-ray diffraction (XRD) patterns were obtained by using a standard DRON-3M powder diffractometer and a Cu K_α (λ_{CuK} = 1.54178 Å) radiation. The data of the XRD patterns were collected in a step-scanning mode with steps of $\Delta 2\theta = 0.025^0$.

3. Results and discussion

Between the crystalline phases of TiO_2, anatase, rutile and brookite, the rutile phase is known as the most stable one. The rutile to anatase phase transformation of the heat-treated TiO_2 powder gel begins around 360 ^oC [12] and the reverse anatase to rutile phase transformation takes place at temperatures higher than 600 ^oC. Small amounts of brookite like impurities were found [13] when the powder was annealed at temperatures higher than 700 ^oC. The TiO_2 anatase crystalline phase is the most appropriate one for a large variety of applications, e.g. photovoltaic devices, photocatalysis, [8,14-16]. The achievement of novel porous TiO_2 based nano-devices becomes plausible from the financial and structural perspective if low cost and controllable sizes of the nanopartiles are firstly accomplished. Therefore, our interest was to determine a procedure that could be further applied to obtain certain sizes of TiO_2 anatase nanocrystallites depending on the desired functionality. In this respect we applied thermal treatments at different temperatures and time intervals.

The existence of the TiO_2 aerogel porous structure was tested by performing SEM measurements. Generally, the morphology of the TiO_2 aerogels can be characterized in terms of two length scales, namely nanoparticles with dimensions of a few nanometers, and mesospheres that have dimensions of a few tens of nanometers and are formed by the close packing of the nanoparticles [10,14]. From the SEM images displayed in Fig. 1 one can evaluate mainly the mesospheres dimensions, which were found to be ~ 30 nm for the as prepared aerogel and ~ 70 nm in the case of the annealed sample. SEM pictures show also the detail of the aerogel aggregation, particularly with regard to the mesospheres, but they do not allow imaging of the nanocrystallites themselves. To measure the size of the nanocrystallites, XRD was proved to be an excellent tool. A good agreement was obtained when the crystallites dimension was evaluated by means of XRD in comparison with that achieved from TEM images [14] and for that reason the first mentioned technique will be further employed in this study.

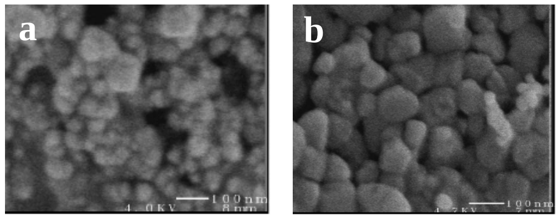

Fig. 1. SEM images of the as prepared (a) and heat-treated at 500 ^0C for two hours (b) TiO_2 aerogel.

Several selected Raman spectra recorded on the aerogel sample annealed at different temperatures for various time intervals are shown in Fig. 2. As can be seen the TiO_2 anatase crystalline phase builds up the aerogels structure as single phase for the samples annealed at 400, 500 and 600 ^oC for different time intervals (1÷5 hours) and gives rise to well-defined bands around 144, 197, 399, 517 and 639 cm^{-1}. Including the superimposition of two fundamental peaks near 517 cm^{-1}, these six peaks correspond to the well-known six fundamental vibrational modes of anatase TiO_2 with the symmetries of E_g, E_g, B_{1g}, A_{1g}, B_{1g} and E_g, respectively [13]. The signature of both anatase and rutile phases was observed in the Raman spectrum of the aerogels annealed at 700 ^oC for one hour, in which the new bands that appear at 447 and 612 cm^{-1} can be certainly attributed to the latter phase. For the samples heat-treated at 700 ^oC for a time interval over two hours a crystalline structure built up preponderantly from rutile phase was found. None of the most intense Raman bands of the TiO_2 brookite, which usually are located around 128 and 153 cm^{-1}, were observed. These results lead to a limitation of the number of the annealed aerogels with structure of pure anatase that will be further investigated.

A close analysis of the Raman spectra of the aerogels annealed at different temperatures reveals some spectral changes that can be associated with modifications of the TiO_2 particles mean size. These spectral changes are not surprisingly at all and refer especially to shifts of a few Raman bands and variations of their half-widths and are more pronounced for the band located nearly the Rayleigh line, around 144 cm^{-1}. All these changes can be discussed in terms of finite size effect of nanocrystallinity. The physical meaning of these spectral changes is mainly based on the fact that in the case of the nanosized materials the wave vector selection rules for optical processes are modified [17,18].

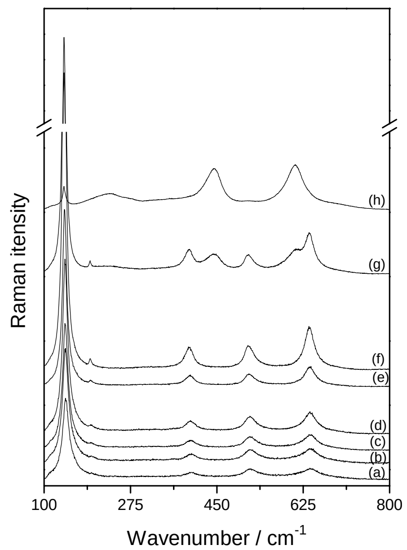

Fig. 2. Raman spectra of the TiO_2 aerogel heat-treated at 400 ^{0}C for 1h (a) and 5h (b), 500^{0}C for 1h (c) and 5h (d), 600 ^{0}C for 1h (e) and 5h (f), 700^{0}C for 1h (g) and 5h (h).

Thus, in comparison with the bulk materials, where only phonons with $k \approx 0$ take part in the Raman scattering process, in the case of nanosized materials, a spread or uncertainty in wave vectors and phonons occurs and thus phonon branch within a range of k values, from $k = 0$ to $k = 1/L$, are Raman active; k representing the phonon wave vector and L the nanoparticle dimension. Because the phonon dispersion curve is not flat the smaller is L, the larger is the shift and broadening of the Raman band. In a previous work, [11] we reported about an experimental correlation between the crystallites mean size L as determined by XRD and the half-width of the 144 cm^{-1} band obtained from the assessment of the Raman spectra of the TiO_2 aerogels annealed for two hours at temperatures between 450 and 600 ^oC. Our results demonstrated that this relationship can be successfully used to monitor the evolution of the TiO_2 crystallites size that build up the aerogels structure by simple measuring a Raman spectrum. In the present study we extend this analysis by annealing for two hours the same type of aerogels at temperatures ranging from 400 to 600 ^oC and than representing the relationships crystallites size-Raman band half-width and band position, respectively. A fit was applied to the experimental data obtained from XRD diffractograms and Raman spectra (the half-width of the 144 cm^{-1} band) [11] according to the following theoretical expressions [10, 17]:

$$\Gamma = \Gamma_0 + k_1\left(1/L^{\alpha}\right) \qquad (1)$$

and

$$\Delta\omega = k_2\left(1/L^{\alpha}\right) \qquad (2)$$

where Γ is the linewidth and $\Delta\omega$ the shift of the band under investigation, while k_1, k_2 and Γ_0 are parameters resulting from the fit. Γ_0 is the intrinsic line-width and α is an empirical Raman-versus-size scaling exponent that was related to the network structure. Both dependencies are depicted in Fig. 3.

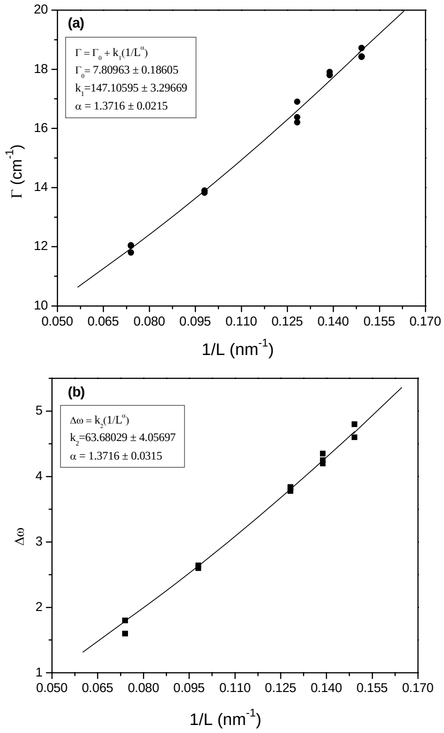

Fig. 3. Correlations between the crystallites mean size (L) determined from the XRD and the linewidth (Γ) (a) and the shift Δω (b) of the 144 cm^{-1} band from the Raman spectra of the TiO_2 aerogel samples annealed for 2h at temperatures between 400 and 600 ^{0}C. Note that in order to avoid the eventual spectroscopic errors that could appear in the linewidth and band position analysis procedure (Lorentzian fit) repeated measurements have been performed.

It was found that for layered materials, such as graphite, α has a value of ≈ 1, while for covalent network semiconductors such as silicon this value is ≈ 1.5 [17]. We found a value of 1.37, which shows that the aerogel structure is more similar with the silicon semiconductor structure. By analyzing the presented dependencies one observes that the variation of the 144 cm^{-1} Raman band half-width is approximately two times more sensitive to the change of the nanosized dimensions of the crystallites than that of the band position. Therefore, the half-width of this band will be used for further investigations.

Once the correlation curve was determined, we decided to further investigate the thermal treatment parameters effect on the anatase crystallites size. Raman spectra were recorded on TiO_2 aerogels annealed at 400, 500 and 600 ^oC for various time intervals (between 1 and 5 hours). The mean size of the crystallites was determined by using the obtained dependency, after a precise assessment of the 144 cm^{-1} Raman bandwidth. The three dimensional (3D) dependency between the crystallites mean size (as determined from the above described correlation), the temperature and time of the thermal treatment is presented in Fig. 4. As expected, one can see that with the increase of the temperature and the time of the thermal treatment a substantial increase of the crystallites mean size takes place. A careful analysis of this representation reveals that the most pronounced effect of the treatment parameters on the crystallites mean size appears for the aerogels annealed at 600 °C, where the largest spread of the crystallites dimension occurs.

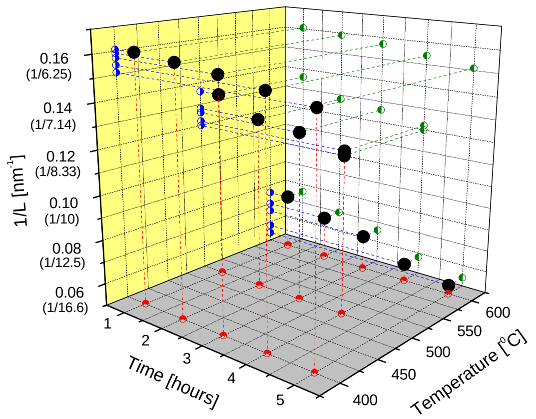

Fig. 4. The 3D dependency between the values of the TiO_2 crystallites mean size, as determined from the Raman spectra analysis, the thermal treatment temperature and time. Note that the values from the parenthesis are representing the mean size (L) of the crystallites that build up the aerogels structure. As an eye-guide the projection of the values on x, y and z-axes are also shown.

Nevertheless, the 3D relationship between the TiO_2 crystallites mean size and the thermal treatment parameters (temperatures and time intervals) should be completed and correlated with other relevant morphological information such as pore mean size in order to completely optimize these porous materials for their further use in various applications. In this respect, efforts are currently done in our laboratories to find the appropriate correlation between the nanometer size of the crystallites and the morphological and structural properties of the TiO_2 aerogels.

4. Conclusions

A semi-empirical model was applied to investigate a series of TiO_2 aerogels annealed at different temperatures and specific information concerning the nature of the aerogels network and correlations between the crystallites mean size and spectral features (position and half-width) of the 144 cm^{-1} Raman band were obtained. Based on these findings the as prepared aerogels were heat-treated at different temperatures (400, 500, 600 and 700 °C) and various time intervals (between 1 and 5 hours) and investigated from the structural point of view by means of Raman spectroscopy. The observed spectral changes were discussed in terms of finite size effect of nanocrystallinity, and a 3D dependency between the crystallites mean size, thermal treatment temperature and time was derived based on the obtained correlations between the crystallites mean size and the half-width of the 144 cm^{-1} Raman band. The optimization of the TiO_2 particles dimension of anatase type can be successfully used for further experiments in which certain sizes of the TiO_2 anatase nanocrystallites are required depending on the desired functionality. The careful analysis of this 3D representation revealed that the most pronounced effect of the treatment parameters on the crystallites dimension appears for the aerogels annealed at 600 °C for different times, where the largest spread of the crystallites dimension occurs.

References

[1] H. Weller, Angew. Chem. Int. Ed. Engl. **32**, 41 (1993).
[2] C. C. Chen, A. B. Herhold, C. S. Johnson, A. P. Alivisatos, Science **276**, 398 (1997).
[3] A. P. Alivisatos, J. Phys. Chem. **100**, 13226 (1996).
[4] H. C. Choi, Y. M. Jung, S. B. Kim, Vib. Spectrosc. **37**, 33 (2005).
[5] S. K. Sinha, Appl. Surf. Sci. **182**, 176 (2001).
[6] M. Tomkiewicz, G. Dagan, Z. Zhu, Res. Chem. Intermed. **20**, 701 (1994).
[7] B. Malinowskaa, J. Walendziewski, D. Robert, J. V. Weber b, M. Stolarski, App. Catalysis B: Environmental **46**, 441 (2003).
[8] S. Boujday, F. Wünsch, P. Portesa, J. F. Bocquet, C. Colbeau-Justin, Solar Energy Materials & Solar Cells **83**, 421 (2004).
[9] G. Dagan, M. Tomkiewicz, J. Phys. Chem. **97**, 12651 (1993).
[10] S. Kelly, F. H. Pollak, M. Tomkiewicz, J. Phys. Chem. B **101**, 2730 (1997).
[11] L. Baia, A. Peter, V. Cosoveanu, E. Indrea, M. Baia, J. Popp, V. Danciu, Thin Solid Films **511-512**, 512 (2006).
[12] P. P. Lottici, D. Bersani, M. Braghini, A. Montenero, J. Mater. Science **28**, 177 (1993).
[13] Y. H. Zhang, C. K. Chan, J. F. Porter, W. Guo, J. Mater. Res. **13**, 2602 (1998).
[14] Z. Zhu, M. Lin, G. Dagan, M. Tomkiewicz, J. Phys. Chem. **99**, 15945 (1995).
[15] V. Danciu, V. Cosoveanu, L. Baia, F. Vasiliu, M. Baia, M. Popa, L. Diamandescu, C. M. Teodorescu, Mater. Sci. & Eng. C, submitted.
[16] V. Danciu, L. Baia, V. Cosoveanu, M. Baia, F. Vasiliu, L. Diamandescu, C. M. Teodorescu, Mater. Sci. & Eng. C, submitted.
[17] C. J. Doss, R. Zallen, Phys. Rev. B **48**, 15626 (1993).
[18] D. Nesheva, J. Opto. & Adv. Mater **7**, 185 (2005).

*Corresponding author: lucb@phys.ubbcluj.ro