Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 25 (2005) 2051–2054

www.elsevier.com/locate/jeurceramsoc

Hybrid organic–inorganic films by assembling of Si–Zr-based nanobuilding blocks

S. Diré[a,*], G. Brusatin[b], M.L. Di Vona[c], P. Egger[a], M. Ferrari[d], P. Innocenzi[e], S. Licoccia[c], P. Romagnoli[f], M. Trombetta[f], L. Zampedri[a,d]

[a] *Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali, Università di Trento, via Mesiano 77, 38050 Trento, Italy*
[b] *Dipartimento di Ingegneria Meccanica, Settore Materiali, Università di Padova, via Marzolo 9, 35131 Padova, Italy*
[c] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, via della Ricerca Scientifica 1, 00133 Roma, Italy*
[d] *CNR-IFN, Istituto di Fotonica e Nanotecnologie, via Sommarive 14, 38050 Povo, Trento, Italy*
[e] *Dipartimento di Architettura e Pianificazione, Università di Sassari, Palazzo del Pou Salid, Piazza Duomo, 07041 Alghero, Italy*
[f] *Centro Interdisciplinare Ricerche Biomediche (C.I.R.), Università "Campus Bio-Medico", via Longoni 83, 00155 Roma, Italy*

Abstract

The possibility of combining inorganic and organic components at the nanosize level in a single material by the sol–gel process has made possible the development of new multifunctional materials. However, the phase interaction between organic and inorganic moieties can be controlled only to a limited extent by using hydrolysis–condensation reactions of metal alkoxides. The preparation of nanostructured organic–inorganic (O/I) materials by assembling of nanobuilding blocks (nbb) allows controlling the extent of phase interaction, which in its turn governs the structure–properties relationships. A suitable method is the preparation of inorganic nanosized preformed objects exploiting the features and the reactivity of functional end-capping organic groups.

We present here the synthesis of Si- and Zr-based nanobuilding blocks prepared by reacting diphenylsilanediol and Si and Zr precursors, with M-OR or M-Cl functions. The non-hydrolytic condensation between silanols and alkoxide or chloride groups has been exploited in order to obtain the Si- and Zr-based nbb. These nanosized objects have been further processed by dip coating for preparing films starting from suitable solutions. The structural characterisation of prepared nbb has been obtained using infrared and nuclear magnetic resonance techniques.

Keywords: Precursors-organic; Films; Optical properties; Organic–inorganic hybrids

1. Introduction

The sol–gel chemistry is an efficient way for designing novel materials with the possibility of combining inorganic and organic components at the nanosize level.[1] However, main drawbacks of the conventional sol–gel route to hybrid nanocomposites stay in size polydispersity and local heterogeneity in chemical composition. Since the control of molecular structures is a fundamental issue for properties tailoring, in the last years, the sol–gel research has been focused on the synthesis of nanocomposites based on inorganic building blocks (nbb), which can build up an inorganic/organic network exploiting the reactivity of functional end-capping organic groups. They have been developed for various systems, like oligosilsesquioxanes and derivatives.[2,3]

This paper presents the synthesis of Si- and Zr-based nanobuilding blocks prepared by condensation of diphenylsilanediol (DPDO) with zirconium tetrachloride, $ZrCl_4$ and trialkoxysilane, $RSi(OEt)_3$. The choice of precursors for nbb preparation is determined by the task of preparing hybrid nanocomposites films with application in photonics. High refractive index and low absorption in the NIR range are the requirements for the final materials. The introduction of phenyl rings bonded to Si and Zr–O bonds should lead to a high refractive index material. The reaction conditions should assure the full condensation, thus avoiding the optical

---

* Corresponding author. Tel.: +39 0461 882456; fax: +39 0461 881945.
E-mail address: sandra.dire@ing.unitn.it (S. Diré).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.010

absorption in the NIR region mainly due to residual OH groups.[4] In a previous work, the non-hydrolytic condensation process was exploited in order to react DPDO and vinyltriethoxysilane (VTES).[5] ATR-FTIR and NMR results showed the almost complete consumption of Si–OH and Si–OEt groups to give cyclosiloxane-based products. According to these positive results, the same synthetic approach is followed in this work, which is addressed to the synthesis of nbb suitable for preparing films by the sol–gel process.

2. Experimental

Reactions were carried out in argon atmosphere using standard Schlenk techniques with dried solvents.

2.1. Zr-nbb

DPDO was dissolved in DMF at room temperature (R.T.) and the solution was cooled down to −65 °C; $ZrCl_4$ was dissolved into the mixture, which was kept at −65 °C for 1 h and afterward slowly allowed to reach R.T. The homogeneous and colourless solution was further stirred for 12 h. The molar ratio between DPDO–$ZrCl_4$–DMF was 1:1:10 and 2:1:20.

2.2. Si-nbb

A modified trialkoxysilane (GTES) was prepared by hydrosilylation reaction of triethoxysilane (TREOS) with geranylacetate (G) in acetone with addition of platinum–divinyltetramethyldisiloxane catalyst. DPDO was mixed with acetone and pyridine (molar ratio = 1:10:2) and the solution was stirred for 2 h at R.T. After Pt catalyst removal, the appropriate amount of GTES solution was added to the DPDO solution (molar ratio DPDO:GTES = 3:2) and the mixture was reacted for one week at R.T. The clear solution was evaporated at 10^{-2} Torr and 50 °C and Si-nbb was recovered as viscous oil.

2.3. Characterization techniques

ATR-FTIR spectra were collected in the range 4000–550 cm^{-1}, on a Nicolet 870 E.S.P. with a Golden Gate MK2 Diamond Specac cell (32 scans, 2 cm^{-1} resolution), and a Magna 550 equipped with ZnSe crystal (4000–650 cm^{-1}). ^{29}Si NMR spectra were recorded with a Bruker Avance 400 spectrometer, operating at 79.49 MHz. Chemical shifts (ppm) are referenced to tetramethylsilane (TMS).

3. Results and discussion

3.1. Zr-nbb

The ability of diphenylsilanediol to react with trialkoxysilanes leading to oligomeric siloxanes has been demonstrated to depend on the synthesis conditions.[6] Particularly, bases greatly influence the condensation ability through the DPDO deprotonation step, thus favouring the nucleophilic attack to the trifunctional Si-alkoxide.

The reactivity towards condensation between zirconium chloride and diphenylsilanediol has been studied in different solvents and with the addition of catalysts. The attempt to use organic bases to catalyze DPDO and $ZrCl_4$ non-hydrolytic condensation was unsuccessful: using pyridine and butyl lithium in THF the condensation product immediately decomposed after preparation. As a consequence of these results, different solvents were used to favour the condensation reaction between silanols and Zr–Cl groups without catalyst addition. When acetone was used a strong band appeared in the FTIR spectrum, due to Si–O–Zr heterometallic bonds. However, the solution was dark red probably owing to the reaction between $ZrCl_4$ and acetone, and the precipitation of a zirconia-based orange solid was observed. On the contrary, the use of dimethylformamide (DMF) allowed obtaining a homogeneous and stable solution. After dissolution of DPDO in DMF, the shift from 902 to 910 cm^{-1} of Si–OH related IR absorption was observed, attributable to the partial Si–OH deprotonation to $Si–O^-$.[7] The addition of $ZrCl_4$ led to a homogeneous solution only at very low temperature (−65 °C). The same reaction run at RT and −4 °C produces zirconia precipitation.

The ^{29}Si NMR spectra of the mixtures obtained by reacting DPDO and $ZrCl_4$ in DMF are shown in Fig. 1. The classical D_m^n notation will be used, where D is a difunctional silicon species; n represents the number of oxo bridges and m, the number of silicon atoms in the cyclic species.

Despite the numerous resonances present, it is not straightforward to assign each one to molecular structures; however, it has been reported that signals due to DPDO self-condensation have a chemical shifts between −46.0 and −46.4 ppm for linear D^2 species, and between −42.3 and −43.1 ppm for cyclic D_4 species.[8,9] Cyclic compounds are, in fact, downfield shifted with respect to linear species due to the reduction of Si–O–Si angle.[10]

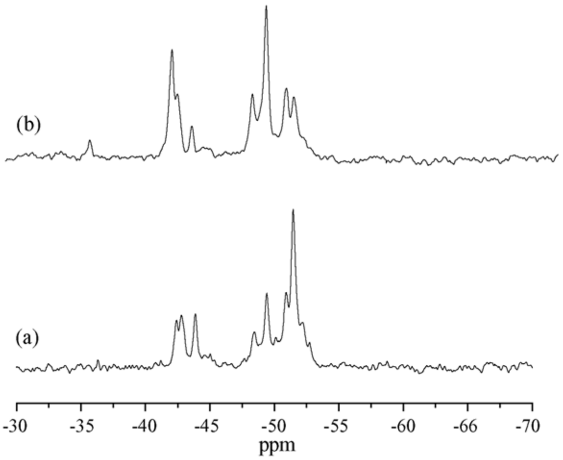

Fig. 1. ^{29}Si NMR spectra of (a) DPDO–$ZrCl_4$ 1:1 and (b) DPDO–$ZrCl_4$ 2:1 in DMF.

In the spectrum of the sample with a 1:1 Si:Zr ratio, two main groups of resonances are observed (trace a) in the spectral region characteristic of D-type signals: between −42.4 and −43.9 ppm and between −48.4 and −51.5 ppm. The first group of signals can be assigned to cyclic self-condensation of DPDO; the upfield shift of the second group of resonances can be attributed to the effect caused by presence of zirconium atoms, and their occurrence is indicative of the formation of a network containing the Si–O–Zr unit in different environments. Cyclic and/or linear cross-condensation compounds may be present, but, despite the wealth of literature existing on ^{29}Si NMR, no reference data have been reported on the solution spectra of similar species. Trace b shows the spectrum obtained by reacting DPDO and $ZrCl_4$ in 2:1 ratio. By comparison with trace a, it is evident that the variations of chemical shifts are very small. The predominant features of the spectrum are the difference in the relative intensity of the resonances and the presence of the signal at −36.3 ppm, due to the D^1 unit.

ATR-FTIR spectra (in the region 1300–600 cm^{-1}) of DPDO–$ZrCl_4$ 1:1 and DPDO–$ZrCl_4$ 2:1 samples in DMF are reported in Fig. 2a and b. Bands due to DMF–$ZrCl_4$ system, mainly dominate both spectra. In order to point out absorption signals due to the condensation products, subtraction results between samples spectra and DMF–$ZrCl_4$ spectrum are reported in Fig. 2d and e.

The shift of Si–O–Si stretching band at 1095 cm^{-1} [11,12] towards lower wavenumbers indicates the formation of Si–O–Zr hetero-linkages. In this regard, the evolution of this band in two components at 1070 and 1050 cm^{-1}, may thus indicate the presence of two Si–O–Zr populations characterized by different environments. Moreover, the absorption signal at 745 cm^{-1} further confirms the presence of Si–O–Zr bonds. The Si–O–Si stretching band at 1120 cm^{-1} could be assigned to DPDO self-condensation product according to NMR results. The intense absorption, centred at about 945 cm^{-1} in the case of DPDO–$ZrCl_4$ 1:1 sample could be assigned to the shift towards higher frequencies of the Si–O stretching band of deprotonated Si–OH groups. However, the attribution of this signal only to silanols is still a matter of debate, since the overlapping with a signal due to Si–O–Zr could also be considered.[13]

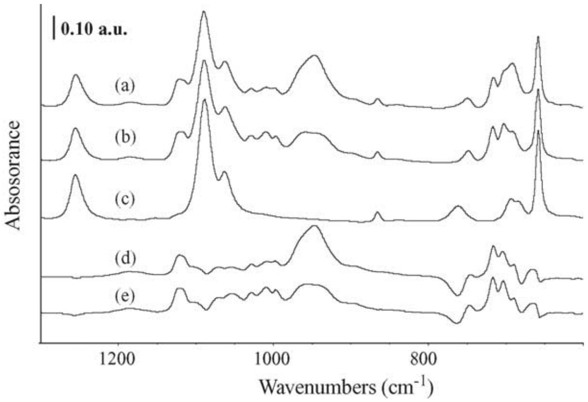

Fig. 2. ATR-FTIR spectra of (a) DPDO–$ZrCl_4$ 1:1; (b) DPDO–$ZrCl_4$ 2:1 and (c) $ZrCl_4$ samples in DMF. Subtraction spectra: (d) = (a) − (c) and (e) = (b) − (c).

The presence in the region 800–695 cm^{-1} of only three bands due to δ_{oop}(CH, Ph) [14] respect sixth, which are expected, and moreover, shifted al lower frequencies, demonstrates that pure DPDO is absent.

Zr-nbb solutions are stable at RT for several days and suitable for preparing films by dip coating or casting on glass sheets. The obtained films are clear, homogeneous and colourless, thickness ranging from 1 to several microns according to the used procedure. Work is in progress to characterize the optical properties of these films.

3.2. Si-nbb

We previously prepared hybrid organic–inorganic films by photopolymerization of nbb based on DPDO and VTES.[5] The results pointed out the impossibility to reach a high degree of condensation of the organic network, probably owing to the steric hindrance generated by the small vinyl function. With the goal of preparing films with improved properties, we have undertaken the synthesis of a Si-alkoxide modified with geraniol (*E*-3,7-dimethyl-2,6-octadien-1-ol), which has been prepared in order to obtain a longer C-chain substituted Si precursor. The possibility to link this organic compound to Si is given by the hydrosilylation reaction (C-silylation), which creates a new Si–C bond. The competitive O-silylation leading to a new O–Si bond was prevented using a protected geraniol, geranylacetate.

The hydrosilylation reaction of triethoxysilane and geranylacetate was followed by FTIR, observing the disappearance of ν(Si–H) and δ(Si–H) at 2194 and 868 cm^{-1} and the appearance of δ(Si–C_{alkyl}) at 789 cm^{-1} as well as the maintenance of ν(C=C) in GTES (1678 cm^{-1}, shoulder) (Fig. 3).

GTES was reacted with DPDO by pyridine-catalyzed condensation. FTIR spectra show the disappearance of signals attributed to Si–OH groups of DPDO and Si–OEt groups of GTES as well as the maintenance of the olefin group of the geraniol tail. By adding Si-nbb to a THF solution

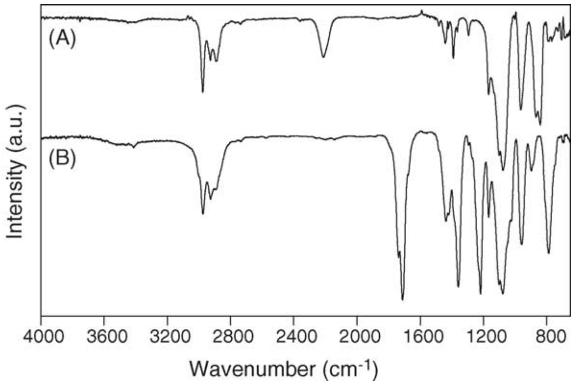

Fig. 3. ATR-FTIR spectra of (A) triethoxysilane and (B) product obtained by hydrosilylation with geranyl acetate.

containing vinyltrimethoxysilane and zirconium propoxide, films were prepared by dip coating on silica glass sheets. The preliminary optical characterization, obtained by m-line measurements in waveguiding configuration, allowed measuring the refractive index and the thickness of films. Films appear homogeneous along the whole surface and the refractive indexes measured in TE and TM polarizations at 543 nm ($n = 1.557 \pm 0.005$) and 633 nm ($n = 1.550 \pm 0.005$) are equal within the experimental incertitude, so that film birefringence can be considered negligible. The film thickness is 1.14 ± 0.05 μm. The films show a good transparency in the range 20 000–4000 cm^{-1} and a very low luminescence band in the range 22 000–14 000 cm^{-1}.

4. Conclusions

Zr-based nanobuilding blocks have been synthesized by non-hydrolytic condensation of diphenylsilanediol and zirconium chloride in DMF. The NMR and ATR-FTIR studies allow describing Zr-nbb as oligomeric species composed of D units involved both in self-condensation and co-condensation with Zr units. The Zr-nbb solutions appear to be suitable for film preparation.

New Si-based nbb have been prepared by condensation between DPDO and a new Si precursor prepared by hydrosilylation reaction of geranylacetate and triethoxysilane. Si-nbb has been used to prepare films, whose thickness and refractive index have been measured by m-line spectroscopy.

Acknowledgement

The financial support of MIUR–COFIN 2002 is greatly acknowledged.

References

1. Sanchez, C., Ribot, F. and Lebeu, B., Molecular design of hybrid organic–inorganic nanocomposites synthezised via sol–gel chemistry. *J. Mater. Chem.*, 1999, **9**, 35–44.
2. Soler-Illia, G. J. d. A. A., Sanchez, C., Lebeau, B. and Patarin, B., Chemical strategies to design textured silica and metal oxide-based organised networks: from nanostructured networks to hierarchical structures. *Chem. Rev.*, 2002, **102**, 4093–4138.
3. Zhang, C. and Laine, R. M., Hydrosilylation of allyl alcohol with $[\mathrm{HSiMe_2OSiO_{1.5}}]_8$:octa(3-hydroxypropyldimethylsiloxy) octasilsesquioxane and its octamethacrylate derivative as potential precursors to hybrid nanocomposites. *J. Am. Chem. Soc.*, 2000, **122**, 6979–6988.
4. Buestrich, R., Kahlenberg, F., Popall, M., Dannberg, P., Muller-Fiedler, R. and Roesch, O., ORMOCERs for optical interconnection technology. *J. Sol-Gel Sci. Technol.*, 2001, **20**, 181.
5. Diré, S., Brusatin, G., Di Vona, M. L., Egger, P., Ferrari, M., Innocenzi, P. *et al.*, Siloxane-based nano-building blocks by reaction between silanediol and trifunctional silicon alkoxides. In *Proceedings of the XII International Workshop on Sol–gel Science and Technology*, 2003, p. 184.
6. Dirè, S., Egger, P., Di Vona, M. L., Romagnoli, P., Trombetta, M. and Licoccia, S., Siloxane-based nano-building blocks by reaction between silanediol and trifunctional silicon alkoxides. *J. Sol-Gel Sci. Technol.*, 2004, **32**, 57–61.
7. Almeida, R. M. and Pantano, C. G., Structural investigation of silica gel films by infrared spectroscopy. *J. Appl. Phys.*, 1990, **68**, 4225–4232.
8. Mayer, B. X., Zöllner, P. and Kählig, H., Characterization of stationary phases for gas chromatography by ^{29}Si NMR spectroscopy. *J. Chromatogr. A*, 1999, **848**, 251–260.
9. Mayer, B. X., Zöllner, P., Rauter, W. and Kählig, H., Characterization of stationary phases for gas chromatography by ^{29}Si NMR spectroscopy II: silphenylene-siloxane copolymers. *J. Chromatogr. A*, 2001, **917**, 219–226.
10. Devereux, F., Boilot, J. P. and Chaput, F., Sol–gel condensation of rapidly hydrolyzed silicon alkoxides: a joint ^{29}Si NMR and small-angle X-ray scattering study. *Phys. Rev. A*, 1990, **41**, 6901–6909.
11. Kamiya, K., Yoko, T., Tanaka, K. and Takeuchi, M., Thermal evolution of gels derived from $\mathrm{CH_3Si(OC_2H_5)_3}$ by the sol–gel method. *J. Non-Cryst. Solids*, 1990, **121**, 182–187.
12. Zhan, Z. and Zeng, H. C., A catalyst-free approach for sol–gel synthesis of highly mixed $\mathrm{ZrO_2}$–$\mathrm{SiO_2}$ oxides. *J. Non-Cryst. Solids*, 1999, **243**, 26–38.
13. Andrianainarivelo, M., Corriu, R., Leclercq, D., Mutin, P. H. and Vioux, A., Mixed oxides $\mathrm{SiO_2}$–$\mathrm{ZrO_2}$ and $\mathrm{SiO_2}$–$\mathrm{TiO_2}$ by a non-hydrolytic sol–gel route. *J. Mater. Chem.*, 1996, **6**, 1665–1671.
14. Ou, D. L. and Seddon, A. B., Near- and mid-infrared spectroscopy of sol–gel derived ormosils: vinyl and phenyl silicates. *J. Non-Cryst. Solids*, 1997, **210**, 187–203.