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Journal of Non-Crystalline Solids 353 (2007) 2826–2831

JOURNAL OF NON-CRYSTALLINE SOLIDS

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Preparation of optical axial GRIN components through migration of charged amorphous ZrO_2 nanoparticles inside an organic–inorganic hybrid matrix by electrophoresis

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Received 23 August 2006; received in revised form 5 June 2007
Available online 9 August 2007

Abstract

A novel sol–gel synthesis route for the preparation of a transparent organic–inorganic nanocomposite was developed by combining methacrylic acid (MA) stabilized, amorphous ZrO_2 nanoparticles, which were synthesized by the sol–gel process, with an organic–inorganic dodecandioldimethacrylate (DDDMA)/3-methacryloxypropyl trimethoxysilane (MPTS) hybrid matrix. The average hydrodynamic particle size was determined to be approximately 6 nm by photon correlation spectroscopy. HR-TEM micrographs present irregular shaped zirconia particles with diameters up to 3 nm. Nearly solvent-free nanocomposites with zirconium (Zr) contents up to 15.2 mol% were synthesized and photochemically cured to transparent crack-free bulks. The surface charged nanoparticles in 1-propanol had an electrophoretic mobility of 0.017 (μm cm)/(V s), measured by Laser Doppler Anemometry (LDA) and a refractive index n_e of $\geqslant 1.648 \pm 0.007$ determined by spectroscopic ellipsometry. After filling the nanocomposite into a linear electrophoresis cell ($1 \times 1.6 \times 0.8$ cm^3), positively charged high refractive nanoparticles migrated through the low refractive hybrid matrix toward the cathode by the application of an electric potential difference of 2 kV/cm for 96 h. A 67% increase in Zr over a distance of 8 mm between the cathode and anode was observed by high-resolution scanning electron microscopy (HR-SEM) and energy dispersive X-ray spectroscopy (EDXS).

PACS: 81.20.Fw; 42.79.Ry; 42.81.Ht; 82.45.–h; 78.67.Bf; 81.05.Mh; 81.05.Ni; 81.05.Pj; 81.05.Qk

Keywords: Colloids; Nanocomposites; Nanoparticles; Organic–inorganic hybrids; Sol–gels

1. Introduction

Currently, GRIN (gradient refractive index) components are needed for a range of diverse application areas. Main fields of application include medical technology (endoscopes), the entertainment industry (CD player, laser diodes, copier, scanner) and optical communication technology.

On the way through a medium with a refractive index gradient, an irradiated beam of light is curved, whereby, at each point of the optical path, the irradiated wave is broken locally according to the law of refraction. This leads to the fact that a beam of light is diverted toward the larger refractive index. In the present work, investigations on axial GRIN components are made. The refractive index of an axial GRIN component changes continuously in only one direction in space (*X*-axis), i.e. at constant *x*-value, the refractive index gradient in *Y* and *Z* directions equals to zero.

GRIN components are produced by various methods. The production method of industrial GRIN lenses, which is used most frequently at present for micro-optics [1,2], is the ion exchange method [3–6]. Messerschmidt et al.

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doi:10.1016/j.jnoncrysol.2007.06.004

produced GRIN lenses of a size below 1.3 mm by Ag–Na exchange with a refractive index difference of maximal 0.145 and a numerical aperture of 0.5 [7]. Disadvantages of this technique are the long production duration, the high energy consumption and the high production costs, respectively, as well as only small lens dimensions of a few millimeters.

Other commonly used methods are chemical vapor deposition (CVD) processes. CVD includes a group of similar processes, e.g. the plasma enhanced CVD (PECVD) process [8–10], the plasma impulse CVD (PICVD) process [11,12] and the photo CVD process [13]. With the PECVD process, layers of 10 μm thickness with a refractive index difference of 0.023 [9] are achieved. However, the disadvantages of the CVD processes are the high production costs by energy-intensive processing, its restriction to the production of layers with limited thickness, as well as difficulties in adjusting the refractive index profiles. Finally the molecular stuffing process [14,15], the wet gel process [16–21] as well as the swollen gel process [22] represent further possibilities to produce GRIN components. Nevertheless, the disadvantages of the former process are the long production duration, the complex processing methods and the high production costs, whereas that of the wet gel process is the long production duration of several weeks, while that of the third process is the small attainable refractive index difference.

Investigations for the production of GRIN components by migration of charged nanoparticles in an organic–inorganic copolymer by an electrophoresis process were carried out so far by Oliveira et al. [23]. The ZrO_2 nanoparticles were synthesized in situ in the prehydrolyzed DDDMA/MPTS hybrid matrix and treated in a cylindrical electrophoresis cell (ring electrode system) with high electric field strengths of approximately 2 kV/cm. A disadvantage of this synthesis route with regard to the electrophoresis process may be the formation of oxidic heterometal bonds Zr–O–Si [24–26] during the nanocomposite synthesis, which may lead to an immobilization of the particles through particle–matrix crosslinking. The photochemical curing process after electrophoresis presents a further difficulty. It was assumed that either a migration of the photoinitiator or a general destruction of the material causes the inhomogeneous curing because of the high electric field in particular in the center of the spherical bulk.

The aim of this work was the development of axial GRIN bulks using the electrophoretic migration of high refractive and positively charged nanoparticles in an organic–inorganic hybrid matrix.

2. Experimental procedures

2.1. Zr-sol synthesis

10.328 g (0.12 mol) methacrylic acid (MA) (Fluka) was added to 37.4 g [corresponding to 0.08 mol zirconium-*n*-propoxide (ZR)] of 70 wt% ZR in 1-propanol solution (Sigma–Aldrich) as a complexing agent. After stirring for 2 h, 160 g 1-propanol (Fluka) was added and stirred for another hour. 2.88 g (0.16 mol) deionized water in 10 g 1-propanol was slowly introduced to the initial solution. After stirring for 3 h, 1.986 g (8 mmol) MPTS was added as a surface modifier and stabilizer. The resulting sol had a molecular ratio Zr/MA/H_2O/MPTS/1-propanol of 1:1.5:2:0.1:37.5. The entire synthesis route is shown in Fig. 2 as a flow diagram.

2.2. Zr-sol characterization

The average diameter of the amorphous ZrO_2 particles was determined by means of high-resolution transmission electron microscopy (HR-TEM; Philips CM200FEG) as well as photon correlation spectroscopy (PCS), i.e. dynamic light scattering (Laser Goniometer ALV/SP-125; Photomultiplier Thorn EMI RFI-QL-30F). The measurements were carried out at a temperature of 20 °C at scattering angles of 60° and 90°. The particle sizes were calculated using CONTIN method.

The electrophoretic mobility of the nanoparticles in alcoholic solutions was measured by Laser Doppler Anemometry (LDA) (Malvern Zetasizer 2000 HS) with a measurement cell for non-aqueous solvents. The wavelength-dependent refractive index of the amorphous ZrO_2 particles was determined by spectroscopic ellipsometry (Sopra ES4G). The sample preparations were made by coating a glass substrate with the unmodified ZrO_2 nanoparticle sol and followed by a drying process in a furnace with 180 °C for 12 h. Since the result was a mixture of the refractive indices of the nanoparticles with inclusions of air and residual solvents, the measured value could only be a minimal refractive index of the particles.

2.3. Nanocomposite synthesis

8.20 g (0.033 mol) MPTS was half stoichiometric hydrolyzed with 0.89 g (corresponding to 0.0495 mol water) 0.1 N HCl. After stirring for 24 h, 11.154 g (0.033 mol) DDDMA was added to the prehydrolyzate and stirred for further 24 h. After that, the methanol content was evaporated by a rotary evaporator (25 mbar; 30 min; 30 °C). The Zr-sol was synthesized in a second parallel process step (Section 2.1). Twenty-four hours after the addition of MPTS to the Zr-sol, 27.82 g of this sol (corresponding to 0.01 mol zirconium) was added to the evaporated, prehydrolyzed MPTS/DDDMA matrix and stirred. The resulting nanocomposite sol had a molecular ratio MPTS/DDDMA/Zr/MA of 3.3:3.3:1:1.5. 0.116 mg (5.7×10^{-4} mol) of the photoinitiator Irgacure 184 (Ciba), equivalent to 0.5 mol% Irgacure 184 per double bond of the nanocomposite, was then added. Additionally, nanocomposites with molecular ratios MPTS/DDDMA/Zr/MA of x:x:1:1.5 ($x = 0.5, 1, 2, 4$) were synthesized through the same synthesis route. Subsequently, an evaporation step followed for each nanocomposite using a rotary evaporator