

# FABRICATION OF GRIN-LENSES BY CONTACTLESS ELECTROPHORETIC-GRADIENT FORMATION IN TRANSPARENT NANOCOMPOSITES

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## 1 ABSTRACT

A new approach to effective radial gradient refractive index (GRIN) lenses has been developed. It is based on the electrophoresis of  $ZrO_2$  nanoparticles with surface charges ( $\zeta$ -potential) in a solvent free organic-inorganic hybrid matrix, synthesized from dodecandioldimethacrylate (DDDMA), methacryl silane (MPTS) and a complex of zirconium n-propylate (ZR) with methacrylic acid (MA). A DC-electric field of 2000 V/cm is applied by a set of ring electrodes on top and bottom of a cylindrical mould containing the matrix sol. The refractive index profile is measured in situ as a function of time by interferometry. The refractive index profile can be conserved by photopolymerisation of the matrix. The resulting refractive index profiles are calculated by computer simulation based on electrophoretic diffusion theory and they are measured by real time Mach-Zehnder Interferometry. The parabolic refractive index gradient of the lenses obtained by variation of concentration of  $ZrO_2$  is in very good agreement with the result of computer simulation. By this method, it is possible to obtain 1 cm radial GRIN lenses with a  $\Delta n = 0.07$  within 5 h.

## 2 INTRODUCTION

In 1854, I.C. Maxwell discovered a new concept for the realization of a perfect optical lens with cylindrical shape by a parabolic gradient index of refraction (GRIN) [1], which was realized for the first time in 1913 by inhomogeneous cooling of a cylindrical glass plate [2]. A glass fibre waveguide with 0.2 mm in diameter became the first commercial GRIN-product, which was produced by ionexchange by Koizumi (NSG) in 1968 [3]. Today, GRIN-materials (glass and polymers) are applied for fibre couplers, telefax machines, laser printers, cameras and endoscopes [4]. Glass GRIN lenses are prepared by Chemical Vapour Deposition [5] and ion exchange in glass [6] and gels [7,8] with subsequent thermal densification. A parabolic index profile could only be realized for small lens diameters (maximum 2 mm [5] to 13 mm [7,8] and processing times of several days [5,6] up to several weeks [7,8] are required to obtain refractive index lifts of about  $\Delta n = 0.1$ . Organic polymer GRIN lenses are produced by the differential polymerization method [9] according to the Colburn-Haines-effect [10], leading to a maximum  $\Delta n$  of only  $10^{-3}$ . In the so called monomer-reactivity-process [11,12], a radial GRIN is produced by centrifugation and subsequent curing of a mixture of monomers with different refractive index and molecular weights. By this process, a lens of 3 mm in diameter with a  $\Delta n = 0.05$  has been obtained. Furthermore, diffusion based GRIN formation in prepolymerized lens bodies has been investigated [13,14] to produce GRIN lenses with diameters of up to 40 mm and  $\Delta n = 0.05$ . However, the practical application of this technique is limited by long processing times of about 2 days. Recently [15], a new concept for the GRIN formation in organic-inorganic nanocomposites (Nanomer<sup>®</sup>) by electrophoresis of surface modified  $ZrO_2$  nanoparticles in a matrix based on methacryloxypropyl trimethoxysilane (MPTS) [16] was developed. The surface charge of the  $ZrO_2$  nanoparticles was adjusted by their  $\zeta$ -potential in the sol, which was filled into a cylindrical mould with concentric Pt ring electrodes on its top and bottom side. The GRIN was formed by application of an electric DC field of 200 V/cm and could be fixed by photopolymerization through the gap of the ring electrodes. In this way, a GRIN lens of 1 cm in diameter with a  $\Delta n = 0.07$  could be prepared within only 5 h [15] which indicates the general advantage of short processing times compared to diffusion based techniques.

However, the direct electric contact between the electrodes and the sol causes difficulties regarding possible electrochemical reactions and poor surface quality after demoulding. Furthermore, the electrical potential function showed strong local maxima in the vicinity of the electrodes [15]. This hinders a simple computer simulation of the GRIN formation process, which would be very interesting for future index profile turning.

Therefore, the aim of this paper was to investigate the GRIN formation in this nanocomposite system with a contactless approach, in order to avoid mechanical post-treatment of the GRIN lenses and to allow a simulation of the GRIN formation process. The general approach was to use thin polymer foils for the electrical insulation of the sol from the electrodes, which would allow a certain discharging of the nanoparticles (as the basis for electrophoresis) but can avoid direct electrical contact to the matrix sol.

### **3 EXPERIMENTAL**

#### **3.1 Sol synthesis**

The materials used to produce GRIN structures were synthesized from methacryloxypropyl trimethoxy silane (MPTS), methacrylic acid (MA), zirconium-n-propoxide (ZR) and dodecandiol dimethacrylat (DDDMA). The  $ZrO_2$  nanoparticles were generated in-situ by hydrolysis and condensation of ZR with MA and water as it has described elsewhere [17-20]. In order to enhance the chain flexibility and hence the mobility of diffusive nanoparticles, the organic monomer of DDDMA was added, which acts simultaneously as a network former during polymerisation of the C=C double bonds. Irgacure 184 was added as a photoinitiator in concentration of 0.2 mol%/mol C=C and the material was photocured by illumination with a Hg-lamp with intensity of 0.6 J/cm<sup>2</sup>.

#### **3.2 Assembling of the electrophoretic cell**

In order to realize a contactless electrophoretic process, the electrodes (a centre electrode dot of 1 mm diameter and two ring electrodes (width 0.5 mm) with a diameter of 4 mm and 2 mm respectively) were deposited on float glass plates by silk screen printing using a commercial silver paste. The so prepared electrodes were covered with a 50  $\mu$ m thick polyester (PE) foil and mounted on the top and bottom side of a metallic cylinder (1 cm in diameter and 1 cm in height). The sol was filled into the mounted cell by a syringe through an opening.

#### **3.3 Characterization**

The variation of the electric potential in the electrophoretic cell was measured with a 100  $\mu$ m metallic point probe [15]. The electrical current during electrophoresis, performed at constant voltage was measured by DM 25XT Wavetek amperemeter.

The refractive index profile was determined in-situ using a Mach-Zehnder interferometer setup [15] with a He-Ne laser (632.8 nm) as light source.

### **4 RESULTS**

#### **4.1 Theoretical aspects**

If insulating foils are used in an electrophoretic cell, the formation of an electric counter potential due to increasing Coulomb interaction between even charged particles approaching each other by the driving force of an electric potential has to be taken into consideration, if a discharging process of the particles at the target electrode (here the centre electrode) is completely prevented. Therefore, the equilibrium distance between two particles was calculated in order to evaluate this model with respect to efficient GRIN formation.

The charge  $q$  of the nanoparticles can be calculated by equation (1), assuming a steady-state movement of the particles, where the force of the outer electric field on the particle is in equilibrium with the friction force (Stokes).

$$q = 6 \pi \eta r \mu = 5 \cdot 10^{-15} \text{ As}, \tag{1}$$

where  $\eta$  is the sol viscosity ( $\eta = 112 \text{ mPa s}$  [15]),  $r$  is the particle radius ( $r = 2.5 \text{ nm}$  [15]) and  $\mu$  is the mobility, which was measured to be about  $7.36 \cdot 10^{-7} \text{ cm}^2/\text{sV}$  by photon correlation spectroscopy [15].

This leads to a charge of about  $5 \cdot 10^{-15} \text{ C}$  (according to about  $10^4$  elementary charges, located in the ligand shell of the particles). With this charge, an equilibrium interparticle distance of about  $R = 80 \text{ nm}$  can be calculated (Coulomb interaction), assuming an external field strength of  $10^3 \text{ V/m}$ , using eq. 2

$$q E = 1 / (4 \pi \epsilon) q^2 / R^2 \tag{2}$$

For a volume fraction of nanoparticles of about 4.45 wt%, an interparticulate distance of only 350 nm can be calculated for the „starting configuration“ of the electrophoretic process which is not much, compared to the „final“ equilibrium distance of 80 nm.

On the other hand, an electric current of about  $1.5 \mu\text{A}$  was measured during the first 5 h of the electrophoretic experiment. This is much less than without the insulating foils, where a current of 67 mA was measured [15] while a similar  $\Delta n$  was achieved, however it would be theoretically sufficient to discharge about  $10^9$  particles per second (see eq. 1).

Therefore it is assumed that the  $50 \mu\text{m}$  thin PE foils cannot completely prevent a discharging of the nanoparticles near the electrodes and that the formation of an efficient counter potential can be neglected in first approximation.

#### 4.2 Measurement of the electrical potential in the cell

In order to be able to calculate the GRIN formation by computer simulation (see 4.3), it was necessary to determine the electrical potential as a function of the radial position in the cell, after it had been shown earlier [15] that a potential gradient in axial direction can be neglected. The result of this measurement is shown in fig. 1.

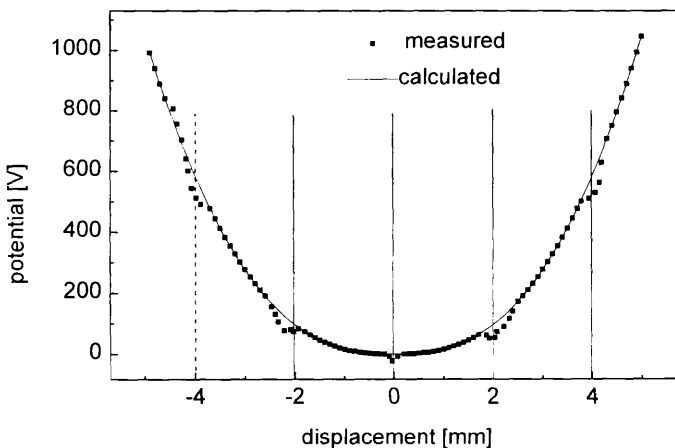


fig. 1: measured potential for the electrophoretic cell with PE foils (see chapt. 3.2) as a function of the displacement with electrodes at the centre, at  $\pm 2 \text{ mm}$  and  $\pm 4 \text{ mm}$  displacement from the center respectively compared to a fitted line.

As one can see from fig. 1, a symmetric and smooth potential curve is obtained. Only small deviations from the fitted line (Potential=  $-10,75 + 0.22x + 26.1x^2 - 0.02x^3 + 0.67x^4$ , where  $x$  is the displacement into the electrophoretic cell) are obtained at the vicinity of the electrodes in the centre and at  $\pm 2$  mm and  $\pm 4$  mm displacement, which indicate a certain charge transfer through the PE foils. This result strengthens the hypothesis, drawn from the calculation of chapter 4.1 that a discharging of the nanoparticles is possible despite the presence of the PE foils. The fitted potential curve of fig. 1 could now be used for the simulation of the GRIN formation which will be described next.

### 4.3 GRIN formation

For the simulation calculation of the GRIN formation, a 2-dimensional model of the electrophoretic cell was applied with respect to the rotatory symmetry of the problem. The cross cut section area of the cell was divided into 10,000 units and 1 positively charged particle per unit was assumed for the starting point of the electrophoretic experiment. Using the measured potential function (see fig. 1) and the measured mobility of the particles ( $\mu = 7.36 \cdot 10^{-7}$  cm<sup>2</sup>/sV [15]), the concentration profile (volume fraction of the ZrO<sub>2</sub> nanoparticles  $c_{ZrO_2}$ ) was determined iteratively, whereby the formation of a Coulomb counter potential was neglected according to chapter 4.1. From this, the refractive index curve was calculated according to eq. (3) [15]

$$n = a c_{ZrO_2} + b, \tag{3}$$

where the constants  $a = 1.765$  and  $b = 1.50$  have been determined by refractive index measurements of appropriate mixtures [15].

The so calculated index profiles could now be compared to profiles, measured after different times of electrophoresis. The result is shown in fig. 2

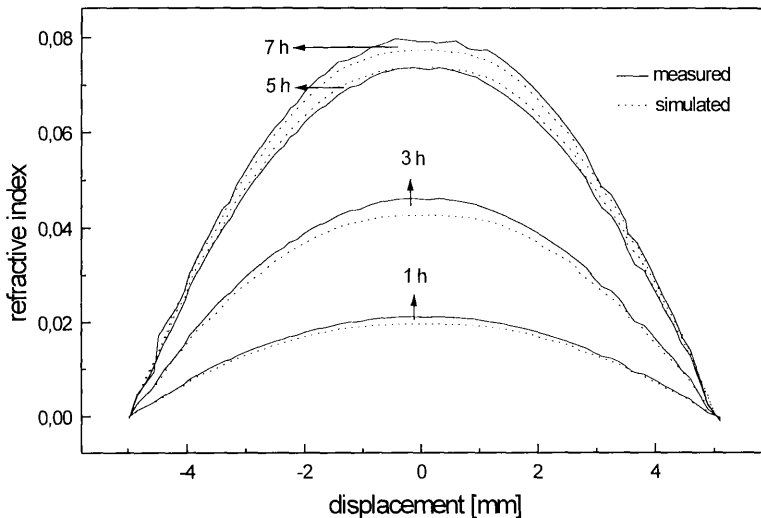


fig. 2: in-situ measured (see 3.3.) and calculated (see 4.3) refractive index profiles in the electrophoretic cell after 1h, 3h and 5 h of the electrophoretic GRIN formation (2000 V/cm).

Fig. 2 shows an excellent agreement between the measured and the calculated refractive index. This again proves the hypothesis of an electrophoretic process of GRIN formation instead of a dielectrophoretic one [21], which one had to consider if the discharging of the particles would be prevented by the PE foils. Furthermore, the refractive index curve shows a nearly

parabolic change, which is suitable for ophthalmic applications [14]. After 5 h, a  $\Delta n$  of 0.07 is obtained, which is the same as obtained in the case of direct electrode contact [15]. In the latter case however, the electric field strengths was only 1/10 (200 V/cm [15]). In order to explain this result, further investigations will be necessary (e.g. drift of matrix components, drop of electrical potential at the PE foils).

The next question was to prepare a solid GRIN lens by photocuring and demoulding and to evaluate the surface quality.

#### 4.4 Preparation of a solid lens

After 7 h of electrophoresis, a  $\Delta n$  of 0.082 was measured in the cell (compare fig.2). The solid lens, obtained after photocuring, was mechanically insable and fell into pieces. Further optimization of the sol composition (more flexible matrix) and the electrophoretic process will be required in order to improve this result. After electrophoresis of only 5 h, a stable lens could be prepared by photocuring and demoulding. The lens is shown in fig. 3.

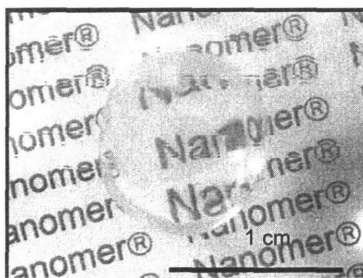


fig. 3: GRIN lens prepared after 5 h of electrophoresis (2000 V/cm), photocuring (UV-irradiation of 0,6 J/cm<sup>2</sup>) and demoulding without mechanical post treatment

As can be seen from fig. 3 the surfaces of the lens are smooth and the GRIN effect is clearly visible. Compared to diffusion driven GRIN formation processes where processing times of several weeks are required to produce a lens with comparable size and  $\Delta n$  [7,8], the electrophoretic method is much faster.

#### 5 CONCLUSION

GRIN lenses with parabolic refractive index profile can be obtained by contactless electrophoresis with thin polymer foils for electrical insulation of the ring electrodes. The fact that the index profile could be simulated very precisely using the measured profile of the electric potential in the cell, opens up very interesting future perspectives for tailoring different index profiles by different potential curves. The electrophoretic method has a high potential for the fabrication of large GRIN lenses in reasonable processing times.

#### 6 ACKNOWLEDGEMENT

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