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Inkjet printing of transparent sol-gel computer generated holograms

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Abstract: In this paper we report for the first time a method for the production of transparent computer generated holograms by desktop inkjet printing. Here we demonstrate a methodology suitable for the development of a practical approach towards fabrication of diffraction patterns using a desktop inkjet printer and nonocrystalline sol-gel ink. In particular, the reported inkjet printing method can be used to generate transparent diffraction structures on supports such as those widely applied in security technologies. Transparent highly refractive layers were deposited with a high precision via a wet-to-dry printing method based on the sol-gel transition phenomenon. With this approach we were able to print a diffraction pattern by TiO2 xerogel, with which a transparent computer generated hologram was created. We argue that this new technology can form the foundation for a new generation of commercial protective coating technologies applied by industrial inkjet printing.

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1. Introduction

The development of additive technologies and materials for security printing holds a great promise for a wide range of industrial applications well beyond the modern printing industry. Despite the great success of modern three-dimensional (3D) printing methods and their growing widespread utilization in different applications, these methods still cannot be routinely used to achieve a resolution below 5 microns [1]. Nevertheless, more advanced approaches based on the layering of materials have recently extended the capabilities of such techniques to the diffraction limit of about 1 micron. Interestingly, this limitation can be in principle overcome by using technologies based on a much more established 1D printing technology. Inkjet printing represents the leading technology among such 1D printing methods [2]. This method is based on the use of liquid ink, which upon contacting with the substrate dries either naturally or with the help of different drying methods (based on infrared (IR), ultraviolet (UV), etc. irradiation) to produce a print [3]. Besides the well-known household and print-industry applications, the inkjet printing method is a well-established technique for the nanofabrication of various structures attracting therefore a great attention from different technological areas including for example the production biosensors [4]. The advantage of this technology is the high accuracy of positioning
of the printed structures along with the clear economic advantages associated among others with the intrinsically low consumption of expensive reagents.

Another advantage of inkjet printing is the possibility of locally applying a strictly predetermined amount of a liquid ink at a high printing speed, up to 244 m/min (for HP industrial printing systems) on a single printhead. Taking into account that considering that the deposition of a printed material does not require additional drying and can be carried out in a single step, such a high printing speed represents one of the key advantages of such technologies compared to those employing photoresists requiring multistage production [5]. Previously inkjet printing has been applied for producing various coatings ranging from conductive transparent films to optical coatings [6]. The development of nanoparticle-based inks allowed expanding [7] the applicability of inkjet printing to fabrication of micro and nanostructured solid objects with a resolution of up to 20 nm along the z-axis [8]. This technological advancement was the result of the unique properties of nanoparticles related to both their small dimensions and specific physico-chemical characteristics, which allow producing uniform layers [9] and induce self-assembly of materials [10] and specific packing on the surface of substrates giving rise to important properties of the resulting materials including new optical characteristics inaccessible to the respective bulk materials.

The utilization of inkjet printing for the production of optical coatings and optical devices is still an underdeveloped technological area. This is primarily due to the intrinsic limitations of the classical method. The principle possibility to obtain optical devices by a controlled deposition of a matter using an inkjet printer would give rise in a near future to a complete new technical field that would enable a roll-to-roll printing [11–14] of optical elements for flexible electronics based on polymer substrates. To utilize inkjet printing for optical applications a number of crucial requirements has to be satisfied, of which the most important are (i) the availability of the inks which can form optically homogeneous structures, (ii) a high ink drying rate to allow the fabrication of three-dimensional microscale structures, and (iii) the specific optical and structural characteristics of the resulting print such as refractive index, low porosity and optical transparency.

Most of these requirements are met by inks made of inorganic compounds that undergo a transition from a sol state in the ink to a solid xerogel state upon drying on a substrate [15]. The use of small nanoparticles in the ink makes it possible to create xerogels having porosity close to that in the bulk materials [16]. When gradually deposited in the form of thin layers, such materials may produce optically uniform surfaces behaving towards light waves as homogeneous layers. Most of the established technologies requiring inks, which can rapidly undergo a liquid-to-solid transition, are based on polymeric substances [4]. However, the utilization of such approaches to the production of optical coatings on polymer substrates is hampered by the high hydrophobicity of the common materials giving to the so-called coffee-ring effects in the prints and, accordingly, to the disruption of optical homogeneity [17]. Furthermore, polymeric inks usually show a low adhesion to films unless additional processing is implemented [18]. Therefore, the development of alternative ink compositions to overcome these crucial limitations represent an important challenge in the field.

Potentially, methods involving the application of a wet hydrophilic layer on a hydrophobic substrate surface enable to cross-link droplets and to decrease their x-y dimension upon increasing the thickness of the layer [19]. Applying solid coatings, even in small sizes, on a wet surface may result in chaotic discontinuities in the dried droplets [20]. In the case of sol-gel systems, there is a gradual increase in viscosity simultaneously with a contraction of a drop or a layer from its edges to the center as the increased viscosity prevents the wet layer from the formation of discontinuities [21]. This approach allows one to obtain objects with a very high resolution of up to 1 micron (in z direction) and, at the same time, to maintain the high performance and scalability [3]. The resolution in the x-y direction is determined solely by the hardware
capabilities of the printer. A sub-micron resolution was demonstrated in the recent studying employing the advanced EHD Printing method [23–25]. This renders a soft lithography of one-dimensional (1D) optical structures a very promising approach for the application in the inkjet technology. We have recently demonstrated the utility of this concept by developing the first interference printing technique [8, 22].

The simplest optical element is diffraction grating from which more complex elements of optical systems can be constructed [26]. Diffraction grating [27] used in monochromators and spectrometers are usually prepared by photolithographic methods. Such elements have high line density and can produce color separation in transmission or reflection mode. This principle is widely used in computer-generated holography [28]. From a pattern of diffraction gratings one can develop an optical device that allows recreating an image in its projection [29] under the influence of, for example, a laser irradiation. A transparent holographic film that recreates an image at a certain angle is the most sought-after approach in the field of holography. Such holograms are widely used in manufacturing security features in banknotes, passports, and other important documents. The production methods involve an embossing process, which implies the application of highly refractive lacquers producing a holographic micro-relief on the substrate [22]. In this study, we for the first time employed this approach for inkjet printing of sol-gel titania inks with high refractive index to produce a transparent computer generated hologram.

2. Materials and methods

2.1. Synthesis of a TiO$_2$ ink

To produce a sol, two solutions were prepared. For the first solution, 16 mL of titanium isopropanoxide and 12 mL of 2-propanol were taken. For the preparation of the second solution, 0.7 mL of nitric acid (70%, AR grade) was added to 100 mL of water, and the mixture was heated to 70 °C, after which the first solution was slowly added to the second one under stirring. The resulting mixture was maintained for 1 hour at 70 °C, then hermetically covered by a film and kept for 4 days at room temperature and under stirring. For the preparation of ink, the initial sol was concentrated 5 times by rotary evaporatoration at 50 °C. Resulting concentrated sol was diluted with ethanol in a ratio of 1 : 3 and used for 10 hours after dilution.

2.2. Inkjet printing

To produce diffraction gratings and holographic patterns, a modified inkjet printer Canon IP2840 with the capability of printing on glass slides was used. Standard printing cartridges were employed, which were filled with the titania-based ink. To print diffraction structures, ITO float glass plates were utilized. Indium tin oxide coated glass slide, rectangular with sheet resistance 15 – 25 Ω/sq, slide (Aldrich). Substrates were sonicated in ultrasonic irradiation (USI) bath, rinsed with isopropanol, and dried in a flow of air.

3. Results and discussion

To produce basic optical components by inkjet printing, we use titania-based inks [8]. A distinctive feature of most sol-gel inks is the ability to adjust viscosity and surface tension by diluting with alcohols [30]. Upon addition of alcohol, viscosity increases due to the destruction of the electrical double layer of the particles and an increase in the coagulation contact forces, which results in the controlled gelation of ink without the formation of aggregates and leads to the decrease in the surface tension of colloids. The current titania inks were characterized by the nanoparticle size of 11.9 nm (dynamic light scattering (DLS) measurements) and ζ-potential of +32 mV. After complete drying, such inks form a thick xerogel containing no organic phases, which in contrast to the methods involving the use of surfactants and thickeners for adjusting
Fig. 1. Inkjet printer single drops of TiO$_2$ on indium tin oxide coated (ITO) glass. Surface tension of the ink 24 nN/m and viscosity 8 cP. a) Scanning Electron Microscopy (SEM) image of a single titania drop; b) Optical image of the same drop; c) High Resolution Scanning Electron Microscopy (HRSEM) image of the drop border; d) HRSEM image of the drop border coffee-ring effect; e) HRSEM drop cross-section on glass substrate with about 300 nm thickness. f) Atomic Force Microscopy (AFM) topography of particles in the center portion of a drop.

rheological properties allows maintaining high optical density and transparency of the coatings. This advantage of sol-gel inks makes them unique for the direct fabrication of the finished products, where one has to produce elements and coatings without the need of further surface treatment. However, the generation of such surface structures is practically impossible when using a commercially-available dispersions of titanium dioxide. In this case, the main problem is the lack of gelation of such structures on the substrate surface and, accordingly, the impossibility to form formation of defined optical structures.

The inks applied to the surface using an inkjet printer form a single drop pattern on the substrate, which passes to a solid state upon drying. This is evident from the micrographs collected in Fig. 1 showing the formation of a solid xerogel on the surface after the solvent evaporation. The printed droplets on the substrate have dense structure consisting of titanium dioxide nanoparticles. Fig. 1(a) shows that a circular shape of the dried drop having an increased border thickness (relative to the drop center part) when applied to a hydrophobic substrate. Nevertheless, this height inhomogeneity does not affect the formation of a dense layer with a high refractive index. Even single-drop layer thickness is sufficient to produce an interference effect in the thin film. This effect is clearly shown in Fig. 1(b). The inner surface of the drop remains uniform and homogeneous, Fig. 1(c, f), and it is composed of particles with a narrow size distribution and a sharp transition to the border effect, Fig. 1(d, e). The ratio between the heights of the border and the center of the drop does not exceed 2. Fig. 1(d) shows that the border portion of the drop has a more dense structure because the drying on the hydrophobic surface results in a rapid shrinking of the drop in diameter due to the increase in viscosity upon the evaporation of the solvent. This leads to the density increase in coffee-ring effect, caused by constrict forces aimed at drop center. This process enables the production of both droplets and thin lines on hydrophobic surfaces. Formation of different layer height is clearly seen in the
cross-section of the sample Fig. 1(e). In addition, it is seen that the formation of small dense xerogel nanoparticles on a glass surface provides a good contact with the glass surface. This ensures that there are no voids between the layer and the substrate and the structure near the surface is similar to that in the bulk layer. This is confirmed by the results of the atomic force microscopy (AFM) Fig. 1(f).

The mechanism by which lines can be created from small droplets implies a delicate adjustment of the drop volume until the distance between droplets becomes critical for coalescence and the droplets merge into a single line. This process occurs simultaneously with the decrease in the line width making it possible to fabricate uniform lines on substrate surface required to achieve diffraction structures. One should note that usually [31] the preservation of the line geometry after drying of the droplets cannot be achieved because of the high concentration of the dispersed phase characterized by the high viscosity and surface tension resulting in the parameter $Z$ beyond the requirements of the inkjet printing conditions [7, 32].

To produce a periodic 1D diffraction grating, pixelated pattern of lines was printed by titanium dioxide on the substrate, Fig. 2(f). The dimension of such lines is close in size to the original droplets.

To compare the quality of the printed diffraction grating in the real testing calculations were performed. To this end, as a model of radiation was taken as close as possible in size laser irradiation source (Fig. 2(b)) that radiates to the diffraction grating (Fig. 2(c)) with duty cycle of 50 and eventually calculated diffraction image model (Fig. 2(d)). A more detailed diagram of the calculation and the actual measurements shown in Fig. 2(a).

Similar images only for the actual measurements are shown in Fig. 2(c-g). The printed grating period of $\approx 59$ microns, which, based on the optical microscopy results, is fully confirmed by calculating the grating order using the diffraction equation (1) [33]:

\[
\frac{1}{\lambda} = \frac{1}{d} \sin \theta
\]

where $\lambda$ is the wavelength of the illuminating light, $d$ is the grating period, and $\theta$ is the angle of diffraction.
Fig. 3. Captured from real image data (Fig. 2(g)) of lines intensity and calculation of diffraction maxima and distance of maxima.

\[ d = \frac{2\lambda \cdot m \cdot L}{D_m}, \]  

where \( d \) is the diffraction grating order, \( \lambda \) is the laser wavelength, \( m \) is the diffraction maximum order, \( L \) is the distance to the diffraction picture, and \( D_m \) is the distance between diffraction maxima of the same order (\(-m; +m\)).

According to the calculations, a diffraction order of \( \approx 58 \mu m \) at a wavelength of 535 nm at a distance of 3 m for all three diffraction orders (Fig. 3) was fully consistent with the data obtained.

The reproducibility and stability of the duty ratio are crucial for multiline printing. When using indium tin oxide (ITO) coated glass as a substrate, we were able to achieve a high reproducibility in printed lines showing a reproducibility level lines period (at duty cycle 50) of \( ca. 59 \pm 3 \mu m \) (Fig. 4(c)). In this example we used drop on demand (DOD) technique on a desktop printer. The obtained values correspond to the duty ratio of 50% (Fig. 4(a)) and optical efficiency of 0.96 and 0.48 according to \( T_{+1}/T_0 \) and \( T_{+1}/T_{-1} \) methods, respectively [34].

The possibility of fabrication of diffraction gratings made of high-refractive index material opens avenue towards a practical technology for creating latent security images. The methodology
Fig. 5. Optical properties of high refractive lines. a) Optical transparency (the right angle of incidence) of titania layer inkjet printed on a glass substrate; b) a photograph of a glass slide with a diffraction grating evidencing its high transparency; c) reflection spectra of titania thin film on glass with 30° tilt; d) refractive indexes (R) [35] of titania thin film on a glass substrate calculated using 
$$R = \left[ \frac{n_1 - n_3}{n_1 + n_3} \right]^2$$, where $n_2$ is the refractive index of the film at the same wave-lengths, and $n_1$ and $n_3$ are the refractive indices for air and fused silica, respectively.

The inkjet printed titania is completely transparent in the visible region (Fig. 5(a)) and when printed on a glass slide is almost invisible on transmittance (Fig. 5(b)). At the same time, printed lines made of titania have a reflectance color (Fig. 5(c)) and are characterized by a high refractive index (Fig. 5(d)).

Next, aiming at creating a computer generated hologram (CGH) based on the laser beam diffraction, we printed a diffraction pattern with a coded image of a circle, Fig. 6. The highly refractive image print on the ITO glass has a clear pattern Fig. 6(d), Fig. 6(f) yet it is completely transparent to visible light. When illuminating the pattern with a laser at a wavelength of 650 nm, the long ranges (8 m) are characterized by the recovery of the holographic image on the projected plane. After the horizontal movement of the glass substrate from one end to another, the recovery of the coded holographic image is observed as the circle is moved from the center of symmetry of the laser in a horizontal direction. The holograms of this type are widely used to produce security transparent images for example in Canadian dollar banknotes.
Fig. 6. Inkjet printing of a computer generated hologram from digital information to holography reconstruction. Source image (circle) was recalculated (Blue line) in the holographic pattern with 600 dpi resolution (g) and printed on an ITO coated glass (d) substrate and hologram has reconstructed by red laser (650 nm) at a distance of 8 m from the substrate (Circle reconstruction at the bottom of the picture). Left, center and right - points of laser illumination on slide in green area of picture (g) printed on slide and corresponding image on projection screen. Ink characterization - a) photograph of used ink with 30 wt.% of sol in ethanol; b) Dynamic light scattering of titania nanoparticle size distribution with mean 11.9 nm particle size and ζ-potencial of +32 mV; c) Transmission electron microscopy (TEM) microphotograph of nanocrystalline titania particles. Printed results - d) SEM microphotograph of inkjet printed pattern on ITO glass; e) Zoom-in part of SEM microphotograph showing the structure of a printed hologram; f) Photograph of transparent glass slide with printed transparent holographic pattern; g) Coded holographic image with part (green) printed on a glass slide.
4. Conclusion

The principle of the sol-gel transition on the hydrophobic substrate surface is a fundamental approach that can be employed for the production of highly ordered diffraction gratings thanks to the possibility of achieving a manifold reduction of the drop size in wet-to-dry printing technologies. This technique allows to generate transparent diffraction gratings and computer generated holograms using inkjet printing. The full transparency of holograms to the visible light renders copying and reading of the images by other devices very difficult with classical methods. The results presented in this paper are anticipated to create a base for the development of new roll-to-roll industrial printing technologies.

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