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Femtosecond Laser-Induced Refractive Index Patterning in Inorganic/Organic Hybrid Films

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The desire to increase the performance of optoelectronic devices has driven research into new, versatile optical materials. Among these, materials combinations composed of organic polymers and inorganic materials have sparked a strong interest due to the wide range of refractive indices that are obtainable. However, in parallel to these materials design and discovery activities, simple, broadly applicable fabrication techniques need to be advanced that are adapted to novel materials systems and allow, for instance, straightforward, large-area manufacturing and integration of 3D photonic circuits. Herein, the use of a 3D direct writing laser technique is proposed to locally enhance the refractive index of a recently developed inorganic/organic molecular hybrid that is only composed of the commodity polymer poly(vinyl alcohol) cross-linked with titanium oxide hydrates, for the creation of photonic structures. A spatially controlled refractive index increase of 0.13 between pristine and laser-treated regions is achieved, with the potential of this adaptable 3D-fabrication technique being demonstrated by manufacturing an optical diffraction grating. Considering that the synthesis and deposition of the hybrid material is water based and does not require toxic heavy metals, the work, thus, provides a processing and materials platform toward environment-friendly, green processing of integrated photonic systems and beyond.

1. Introduction

In the everlasting race to improve the performance of optoelectronic devices, polymers have sparked great interest[1–4] thanks to their chemical versatility that can be combined with qualities such as lightweight, mechanical toughness, ease of fabrication at lab and industrial scale, and the potential for low-cost processing. Given that neat polymers generally display low refractive indices, since the early 1990s, incorporating inorganic materials with a high refractive index (HRI)[4–12] within plastic-based matrices has been a widely used strategy to realize HRI nanocomposite systems.[13–17] To overcome problems of inhomogeneous mixing that can lead to scattering losses, molecular inorganic/organic hybrids were introduced, where the inorganic and organic phase can typically not be distinguished. Accordingly, the presence of the inorganic species still leads to an increase in RI while keeping the light transmission high (no light scattering occurs as no nanoparticles or aggregates form) and the chromatic dispersion low.[18,19] Such hybrids offer many opportunities for optical device engineering, and they may pave the way for the straightforward design and fabrication of high-performance 3D photonic circuits, provided a suitable index patterning procedure is identified. The reason is that the overall light management in photonic devices requires precise patterning of the refractive index, ideally in two or three dimensions. To achieve this, so far, different materials and complex deposition, growth, or lithography techniques have typically been used.[20,21] A

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simpler approach is based on direct laser writing, which is widely used to pattern the refractive index of a given material system in a single step and in 3D, without the need for masks that can be expensive. However, in neat polymers such as poly(methyl methacrylate) (PMMA), this approach has provided only a minor RI enhancement ($\Delta n \approx 10^{-4}$ to 10^{-3}),[22–29] reaching up to $\Delta n \approx 10^{-2}$ when, e.g., using hydroxyethylmethacrylate (HEMA)-based or silicone-based ophthalmologic hydrogels. Other notable examples are hybrid materials based on transparent epoxy and/or methyl methacrylate resins containing small silicates[30] and silicate/zirconate clusters.[31] Femtosecond laser patterning of these sol–gel precursors allowed to obtain complex photonic structures with resolution down to 0.2 μm thanks to the high numerical aperture (NA) of the objective lens required to implement the two to three multiphoton polymerization writing techniques. However, these photopolymerizable hybrid resins require a washing step to eliminate unreacted sol–gel precursors and are limited in the achievable absolute refractive index[32] of ≈1.5–1.6, leading to a maximum RI modulation of $\Delta n \approx 10^{-2}$.[33] Although this RI difference may be of interest for some applications, it is still too low for many frontier implementations in the integrated photonics area where having a high phase difference between two or more optical beams along very short geometric paths is crucial.[34] Here, we demonstrate the relatively high-resolution local enhancement of the refractive index by ultrashort pulse direct laser processing in solution-processable inorganic/organic hybrid materials, thus approaching the requirements for use in high-efficiency photonic devices and possible integration with standard light generation or sensor applications (e.g., LEDs, CCD/CMOS).[4] As model system, we selected an organic/inorganic hybrid material formed from poly(vinyl alcohol) (PVAl) cross-linked with different contents of titanium oxide hydrates[19] to cover a broad RI range, prepared with a water-based sol–gel method and deposited by spin coating starting from an aqueous solution. Through femtosecond laser micromachining, a large increase of the local RI ($\Delta n \approx 10^{-1}$, up to $n = 1.86$ at 550 nm) with a transmittance >90% over the entire visible wavelength regime is obtained in the irradiated regions. Furthermore, as a proof-of-concept device, we fabricated an optical grating created from alternating laser-processed and pristine regions. As our technique is based on multiphoton absorption process, similar to the two-photon polymerization phenomena reported by Serbin et al.,[30] it promises future production of 3D bulk structures with submicrometer resolution. Indeed, reaching a third dimension is so far only restrained by the inability to grow thick samples, but when overcoming this limit, the opportunity to realize—in a single step—3D photonic circuits buried in a given material system will be opened.

2. Experimental Results

In order to scrutinize 3D laser machining as a methodology toward complex photonic structures, we selected titanium oxide hydrates/PVAl hybrids as model material system for RI patterning because it has been shown that this hybrid material's RI can be readily tuned via its composition and heat exposure. Indeed, an increase of the RI of up to 1.83 at 550 nm, induced upon a thermal treatment (multistep annealing on hot plate at 150 °C), has been reported,[19] achieved for a material of 60 vol% inorganic content. For such a hybrid material, e.g., made from $TiCl_4$, the change in refractive index was attributed to the thermal activation of further hydrolysis and condensation reactions of OH and Cl groups present in the pristine hybrid material. These reactions lead to the release of water and hydrochloric acid molecules which, in turn, results in a densification and thickness contraction of the hybrid.[35]

Here, we prepared hybrids of broad range of compositions (PVAl with 0, 20, 60, and 80 vol% titanium oxide hydrates) and prepared films with thicknesses ranging from 0.8 to 1.5 μm by spin coating on a glass substrate (see Experimental Section for details). Large areas of $5 \times 5\ mm^2$ were processed by femtosecond laser micromachining as schematically shown in **Figure 1**A, with the relevant physicochemical principle of the laser-induced modification process highlighted (see dashed zoom). The modification induced in the HRI inorganic/organic hybrid material by the ultrashort-pulsed laser light was then assessed.

Already by eye, a uniform change is observed in the irradiated area of the inorganic/organic hybrid material (Figure 1B) when using a laser energy density of $2\ J\ mm^{-2}$ ($P_{avg} = 40$ mW, constant density of 100 000 imp mm^{-1} and a distance between two pattern laser lines of 4 μm), while no changes are observed in neat PVAl upon the same treatment. A more detailed discussion of how the various laser parameters affect polymer modification is reported in the Figure S1, Supporting information. Reassuringly, we find that the material reduces its thickness (by about 25%) during irradiation (Figure 1C).

Our observations suggest that the ultrashort laser pulses promotes the localized raise the temperature in combination with the fast breaking of chemical bonds inducing a considerable increase in the density of our material. The photon energy that we use is, however, well in the transparency region of our titanium oxide hydrates/PVAl hybrid material (absorbance $<10^{-4}$ at 430–1800 nm, with a sharp absorption onset below 350 nm only that depends in intensity on the inorganic content). This suggests that light absorption may occur via a multiphoton transition (titanium oxide hydrates have a bandgap of ≈3.6 eV,[18] indicating at least a two-photon process), which would have interesting consequences for the direct writing of high space resolution 3D patterns. Indeed, as recently reported in a theoretical study by Rahaman et al., the area heated by the interaction between ultrashort pulses and polymeric materials remains highly confined to the volume of the laser spot.[36] This is a typical advantage when using subpicosecond pulses with respect to nanosecond or longer laser pulses.

Importantly, the observed volume change can be expected to result in an increase of refractive index, analogous to the scenario when titanium oxide hydrates/PVAl hybrids are thermally annealed on, e.g., a hot plate. The reason is that the reduction in thickness leads to a densification of the material and, in turn, an increase in refractive index. Thereby, the extent of the observed thickness reduction and, thus, increase of RI (as discussed in detail below), can be manipulated via the hybrid material's composition, with more shrinkage and a higher RI change being observed for high inorganic content systems. This comes without loss in light transmittance. Indeed, a high transparency

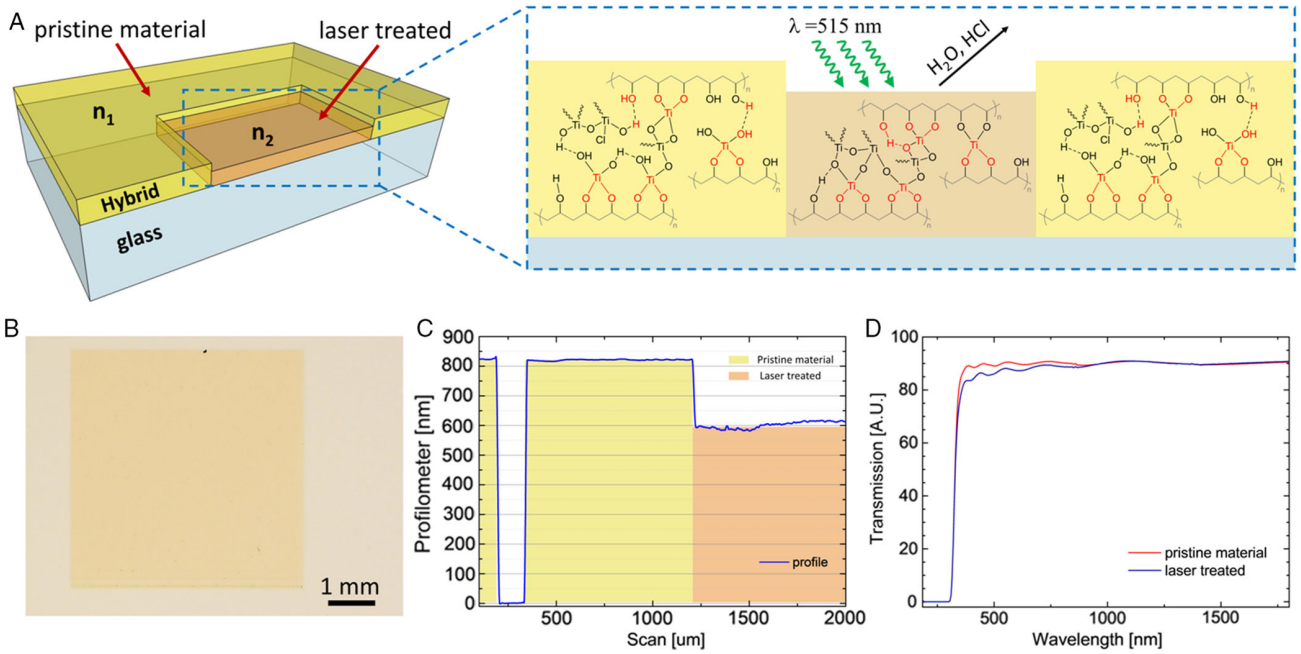

Figure 1. A) Schematic illustration of a patterned HRI molecular hybrid deposited on a glass substrate (left) and depicting the change in the material's chemical structure in the irradiated areas through the loss of water and hydrochloric acid molecules, which results in densification (right). Atoms/moieties that can take part in these reactions during hybrid formation are highlighted in red and bold black. B) Optical image of the area modified by irradiation with ultrashort laser pulses. C) Profilometer data highlighting the change in film thickness upon irradiating a hybrid system comprising 60 vol% titanium oxide hydrates. Pristine areas are highlighted in yellow, while the laser-treated regions are shown in orange. D) Optical transmission measured on a titanium oxide hydrates/PVAl hybrid film (60 vol% inorganic content) before and after laser modification, demonstrating that the laser writing does not affect the high optical transition of the hybrid material.

is kept upon 3D writing. The resolution that can be achieved with our laser processing technique is directly connected to the objective used. With a higher magnification objective, it is possible to bring the vertical resolution closer to the micrometer condition (in the best case and in the absence of optical aberrations), which will be necessary to perform 3D modifications in thicker hybrid materials films. In the case of out-of-focus conditions, we can assume that the modification in the vertical dimension (thickness) is uniform. Similar reasoning applies for the transversal resolution. The horizontal dimension of the line clearly depends on the laser writing setup and parameters (as shown in Figure S1, Supporting Information). At present, uniform, individual lines with transverse dimensions of less than 1 μm were achieved via laser writing when the beam was focused inside the substrate (Figure S2, Supporting Information). By using higher magnification objectives, it is expected that the transverse resolution can be further increased up to the submicrometer scale as shown with two photon polymerization (2PP).[30]

The optical transmittance remains comparable with neat PVAI: >90% in the wavelength regime of 360–1800 nm, as shown in Figure 1D, unless at extreme contents of titanium oxide hydrates (≥80 vol%), where the pronounced and rapid shrinkage can lead to cracks in the polymer surface and, therefore, a reduced transparency. This may be prevented through prolonged aging or plasticization of the material during writing.

To quantify the change in optical properties beyond transmittance, we measured the refractive index dispersion via variable angle spectroscopy ellipsometry, as schematically depicted in **Figure 2**A. First, data of the bare substrate were acquired so that the bilayer structure of a hybrid film on a glass substrate could be taken into account during fitting. Values for the amplitude ratio, Ψ, and phase difference, Δ, were acquired between 370 and 1700 nm, at angles, Φ, of 65°, 70°, and 75°. The optical transmission was also collected and merged in our fitting procedure to improve the model and the RI determination. After prefitting of the thickness (supported by profilometer thickness measurements), the experimental data (Ψ, Δ, and *T*) were fitted using an extended Cauchy model. The quality of data analysis was assessed by the value of the mean squared error (MSE) and by evaluating the agreement level between model and experimental data.[37] MSEs between 1.2 and 2.1 were deduced for pristine (i.e., laser unmodified) inorganic/organic hybrid films, while for laser-treated samples slightly higher MSE values were obtained that increased with titanium oxide hydrates content: 7.56 for a hybrid of 20 vol% inorganic content, to 21.18 for a material comprising 60 vol% titanium oxide hydrates (see Figure 2). Encouragingly, each fit is in broad agreement with the experimental data. [Note: The high frequency oscillations present in the transmission data between 800 and 1000 nm are noise artifacts introduced by the instrument and, thus, were neglected.]

Having established the suitability of our fitting model, we extracted the refractive index dispersion for the various hybrid thin films, pristine and laser-treated. **Figure 3**A summarizes the refractive index values obtained for the different systems.

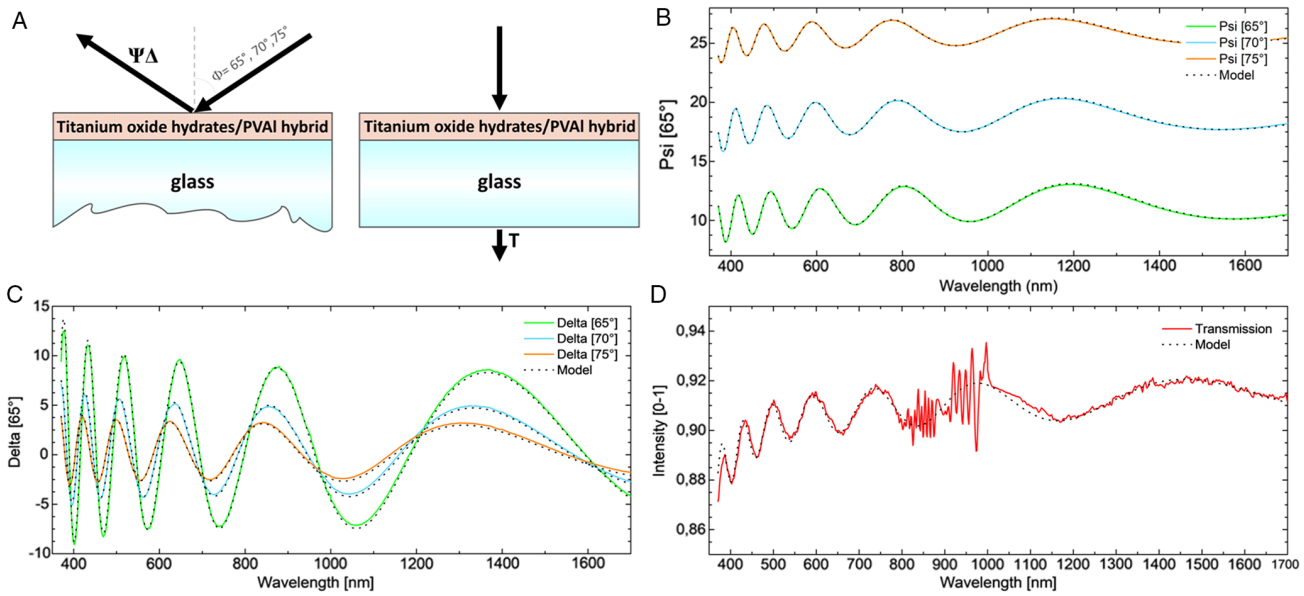

Figure 2. A) Schematic illustration of the spectroscopic ellipsometry measurements performed at specific angles (left) and at normal incidence (right) to obtain the light transmission through a specific sample, required for data fitting. B,C) Comparison between model (dot lines) and experimental data (continuous coloured lines) of spectroscopic ellipsometry and D) transmission of titanium oxide hydrates/PVAl hybrid films (20 vol% inorganic content).

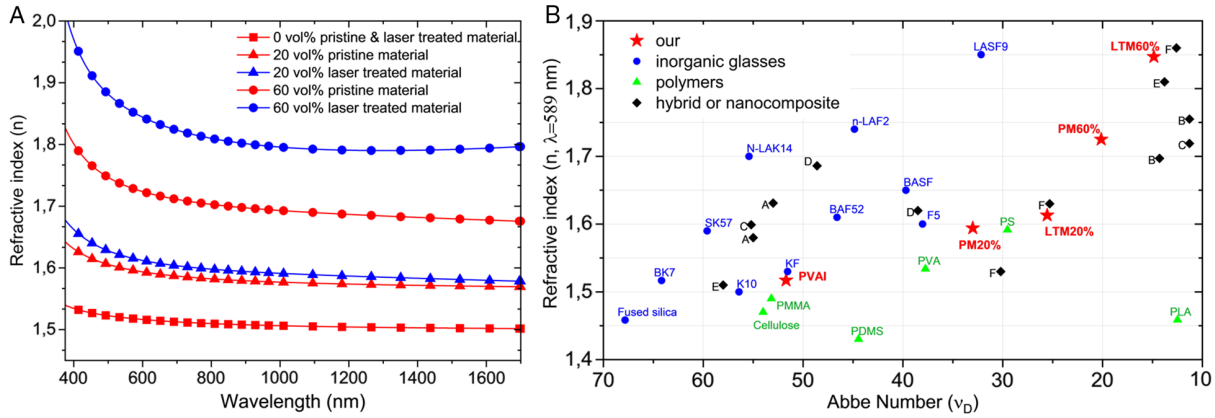

Figure 3. A) Refractive index of titanium oxide hydrates/PVAl hybrid films of different compositions, pristine (red lines) and after laser pulse treatment (blue lines). Laser- treated and pristine materials at 0 vol% concentration (i.e., neat PVAl) feature the same refractive index. B) Abbe diagram comparing different materials from literature with the present work: (red) hybrid films presented here [PM = pristine material; LTM = laser treated material; X% = vol% inorganic content]; (blue) inorganic glasses; (green) common polymers; (black) polymer-based hybrid materials or nanocomposites reported in literature [A = Ref. [42]; B = Ref. [41]; C = Ref. [43]; D = Ref. [3]; E = Ref. [6]; F = Ref. [44]].

The RIs for pristine (i.e., laser unmodified) titanium oxide hydrates/PVAl hybrids are shown in red, while in blue the RI dispersion traces are shown for films that have undergone laser processing. Several observations can be made. In agreement with literature on such hybrid materials,[18,19] we find that the RI increases with titanium oxide hydrates content, both for the pristine materials and laser-written samples. We like to emphasize that the 60 vol% titanium oxide hydrates/PVAl hybrid in its pristine state features an intrinsically higher RI compared to, e.g., hybrid materials based on methyl methacrylate (MMA) resins containing silicates and zirconates as inorganic components because of an overall higher molar ratio of inorganic to organic species[33] ($n_{\mathrm{TiO}x/\mathrm{PVAl\ 60\ vol\%}} \approx 1.73$ with molar ratio of titanium oxide hydrates:PVAl of 1.1:1 vs $n_{\mathrm{SZ2080}} \approx 1.53$ with molar ratio of silicates/zirconates:MMA of 2:1). We attribute this observation to the higher volume concentration of the inorganic species achieved in titanium oxide hydrates/PVAl hybrids with respect to the MMA-based hybrid resins, which is likely due to the lower molar volume, V_m, of our polymeric matrix[38] ($V_{m,\ \mathrm{PVAl}} \approx 34\ \mathrm{mL\ mol^{-1}}$ versus $V_{m,\ \mathrm{PMMA}} \approx 87\ \mathrm{mL\ mol^{-1}}$). This view is consistent with the remark that the RI increase is more pronounced for the higher inorganic content systems. An increase of 1.3% is observed for titanium oxide hydrates/PVAl hybrids of an inorganic content of 20 vol%, compared to 7.5% found for

materials with 60 vol% titanium oxide hydrates, reaching a value of 1.86 at 550 nm in the case of the laser-processed hybrid system. Moreover, the high repetition rate used during fs patterning promotes localized accumulation of heat in combination with rapid breaking of chemical bonds.[39,40] This can be expected to drive the condensation reaction between the polymer and the titanium oxide hydrates precursor leading to densification. We indeed can directly relate the large RI change induced by patterning, e.g., the 60 vol% hybrid with the pronounced densification obtained in the laser-irradiated areas of the material, as mentioned above. [Note: The densification of the hybrid is significantly more pronounced than what is found for fs-patterned hybrid MMA resins.[32,33] This is because the condensation reactions that occur in the titanium oxide hydrates/PVAl hybrids involve a substantial loss of matter, as opposed to MMA-based hybrid resins such as SZ2080, which seem to merely be subjected to chemical shrinkage.[31] Indeed, while our material undergoes 25% contraction in laser-treated areas, MMA hybrid resins shrink by ≪8–10%.]

Finally, to evaluate the optical quality of various inorganic/organic hybrid films, pristine and laser patterned, the value of the Abbe number, ν_D, was calculated. As ν_D is a parameter that measures the dispersion of the refractive index in the visible region, a low value may suggest chromatic dispersion. It is known that the refractive index and the Abbe number are generally related; the trend is that HRI materials show smaller ν_D values. Specifically, polymer-based materials with RI > 1.70 have usually Abbe numbers below 20.[41] As shown in the Abbe diagram (Figure 3B), our hybrid polymer films (red stars) follow the same behavior, with a decrease of the Abbe number and an increase of RI with inorganic content. Furthermore, the values of refractive index and Abbe number that we obtained (i.e., RI = 1.72, $\nu_D = 20.1$ for the pristine hybrid 60 vol%, and RI = 1.85, $\nu_D = 14.9$ for laser-processed films) are on par with state-of-the-art materials,[3,6,41–44] with the additional benefits offered by the possibility to locally modify material properties, inducing a large Δn, and the use of solution-processing method. The relatively high RI dispersion in addition will increase the optical phase difference in short pathways (such as OPD interferometers[34] or compact and portable spectrometers), assisting in exploiting the coupling of this type of hybrid material and fabrication technique.

In order to illustrate the potential of laser writing titanium oxide hydrates/PVAl hybrids for device fabrication, we designed and produced a 10 µm-pitch thin optical phase grating within a 5 × 5 mm^2 area. The grating, operating in transmission mode, ensures multiorder diffraction behavior that is symmetrical with respect to the zero order, as shown in **Figure 4**E. Figure 4A shows the schematic representation of the laser writing grating process, while Figure 4B shows the written surface profile of the lattice. As can be observed (Figure 4B), the realized grating is composed of two periodic structures aligned along the *z*-axis: one in relief (air–pristine material) and one completely inside the substrate (laser treated–pristine material). While the nonirradiated areas inside the pattern are slightly lowered compared to the pristine film, most likely due to tensions generated by the shrinkage of the nearby areas, the device quality achieved over larger areas is excellent as the optical

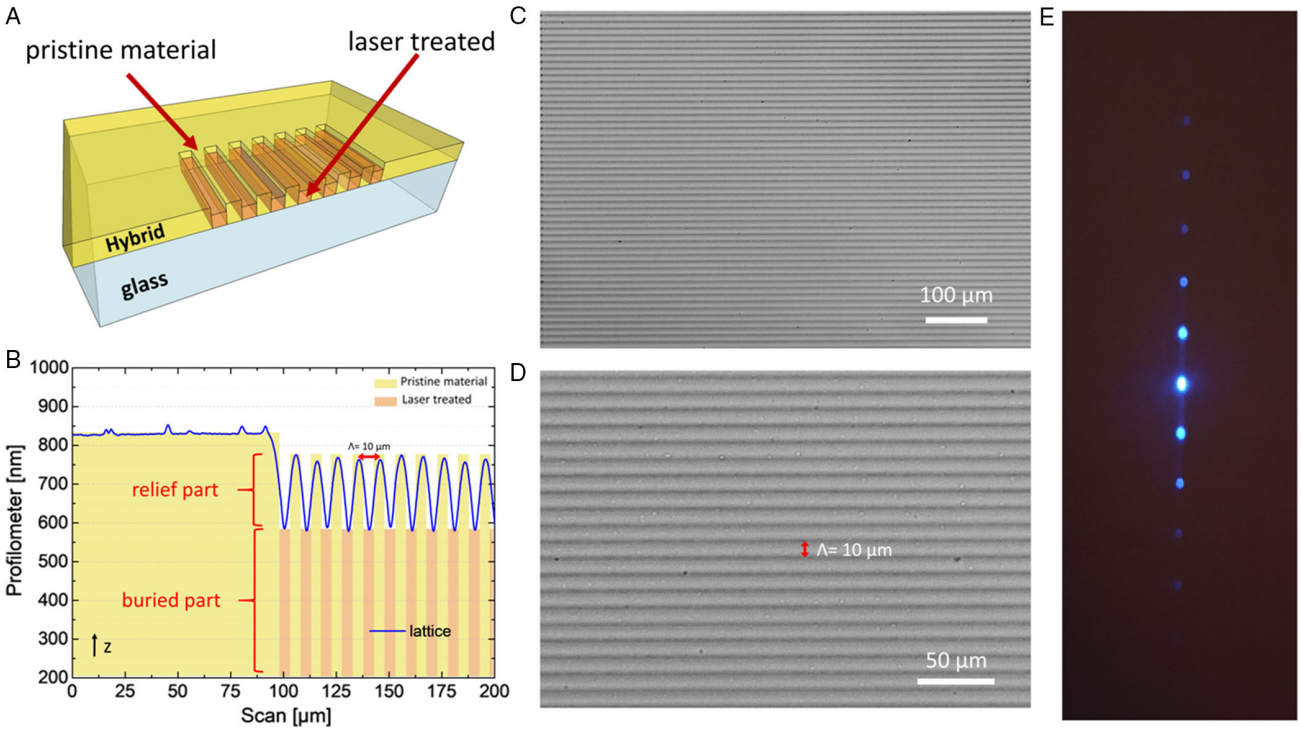

Figure 4. A) Schematic illustration of the diffraction-grating fabrication process using titanium oxide hydrates/PVAl hybrid thin films (60 vol% inorganic content). B) Profilometer data measured on the produced grating. C,D) Optical micrographs of the grating pattern realized via femtosecond laser micromachining. E) Diffraction pattern created by a laser beam impinging on this grating structure.

micrographs presented in Figure 4C,D illustrate. Although the calculation of the diffraction efficiency is complex in this specific case-in-point (and, thus, is beyond the scope of this work), under certain boundary conditions, the Raman–Nath theoretical model can describe its efficiency. Taking into account our data (Δn and thickness differences), the theoretical maximum efficiency is in the range of 2–4%, while the experimental value obtained is in the range of 1–2%. This result emphasizes the excellent RI–control capability offered by the proposed fabrication technique.

3. Conclusions

HRI inorganic/organic hybrid materials that can be produced via a water-based sol–gel method were used to assess the suitability of laser writing to create refraction index patterns. A maximum enhancement in RI of 0.13 with an ultrafast laser pulse in a hybrid comprising 60 vol% titanium oxide hydrates has been reached while not affecting the material's optical transparency (a light transmission of >90% is maintained in the laser-written samples). We tentatively attribute the fact that this specific hybrid material can be laser patterned despite the low light absorption in the visible wavelength regime to multiphoton absorption phenomena, which seems to assist in spatially inducing a refractive index change at accurate locations in three dimensions (with our setup we realized a spatial resolution of $\Delta_{xy} \approx 1\,\mu m$, see Figure S2, Supporting Information). This highly desirable feature may, thus, allow the future manufacturing of complex 3D photonic circuits with the only limitation given by the diffraction of the optical laser system used and the hybrid film thickness. For the latter, the advancement of other fabrication methodologies, e.g., melt processing,[18,35] should enable the realization of structures thicker than 10 μm and targeted toward the fabrication of 3D photonic circuits. This is, however, beyond the scope of this work. As a proof of concept, we fabricated a simple optical diffraction grating using a hybrid comprising 60 vol% titanium oxide hydrates, thus providing a good compromise in the RI change that can be achieved and the resulting optical quality of the film. The combination of a new, versatile, and water-processable inorganic/hybrid material produced in a green fashion (especially if precursors other than $TiCl_4$ are used[45]) and the controlled, local increase of the refractive index using femtosecond micromachining could emerge as a method of manufacturing complex photonic circuits or other industrial optical applications, such as photonics wire bonding.[46]

4. Experimental Section

Materials: Titanium(IV) chloride (ReagentPlus; purity >99.9%) and PVAl (Mowiol 18-88; weight–average molecular weight, $M_w \approx 130\,kg\,mol^{-1}$; residual content of acetyl groups = 10.0–11.6%) were purchased from Sigma-Aldrich. MilliQ water was used for the inorganic/organic material synthesis via a sol–gel route.

HRI Polymer Film Preparation: Stock solutions of titanium oxide hydrates[45] of 1 or 2 M, depending on the final viscosity needed, were initially hydrolyzed. Hybrid solutions of different titanium oxide hydrates content (with respect to the PVAl) were prepared by introducing corresponding amounts of titanium oxide hydrate stock solution to a $40\,g\,L^{-1}$ aqueous solution of PVAl under stirring. The temperature of the mixture was kept around 4 °C (measured with a thermocouple and keeping the temperature using an ice salt bath) to slow down the hydrolysis reaction between titanium oxide hydrates and PVAl. This ensures that a high-transparency, optical low-loss molecular hybrid material is formed with the titanium oxide hydrates species cross-linking the polymer component rather than forming TiO_2 nanoparticles. Titanium oxide hydrates volume fractions in the final hybrid material were calculated as previously reported.[18] Prior to deposition, glass substrates were sequentially sonicated in acetone, isopropanol, and milliQ water for 15 min, air-dried and before they underwent a 10 min UV–O_3 cleaning step. Solutions were then spin-coated on glass substrates with speeds between 800 and 2000 rpm and air dried at room temperature for up to 2 h. The produced films were subsequently stored under vacuum for a week to complete the ageing process,[19] leading to the elimination of hydrolysis side products such as HCl and H_2O.

Laser Micromachining: The laser micromachining system used for the RI patterning is based on a 10 W amplified femtosecond laser source (Light Conversion, Pharos) characterized by pulses duration of 240 fs, a fundamental wavelength of 1030 nm, and a repetition rate ranging from 1 kHz up to 1 MHz. The polymer modification was achieved using the second harmonic laser line (515 nm) with a 500 kHz repetition rate and an average power of 40 mW. To uniformly RI pattern an area of $5 \times 5\,mm^2$, the laser light was statically focused 50 μm over the hybrid film surface using a telecentric microscope objective (10×, NA = 0.21, Mitutoyo). The writing parameters were carefully set to avoid any ablation mechanism. The 2D patterns were obtained with constant energy density writing ($100\,000\,pulses\,mm^{-1}$) synchronizing the pulses with the dynamics of the trajectories (speed and acceleration). Samples were placed on a computer-controlled 3-axis high-resolution (<50 nm) air-bearing translation stages (ABL-1000, Aerotech). For a more detailed discussion of how different laser parameters (pulse energy, repetition rate, writing speed, and spot dimension) will affect material modification, we refer to Figure S1, Supporting Information.

Polymer Characterization: The sample thickness was assessed using a contact profilometer (Veeco Dektak 150). The light transmittance through titanium oxide hydrates/PVAl hybrid films was measured using a UV/vis/NIR spectrometer (LAMBDA 1050, PerkinElmer); the spectra were acquired between 185 nm and 1800 nm in 5 nm steps.

The refractive index of the polymer was determined using a variable angle spectroscopic ellipsometer (M2000V, J.A. Woollam Co.). Data were acquired between 370 and 1700 nm (1.5 nm steps) and at angles, Φ, of 65°, 70°, and 75°. Transmission measurements were in addition performed with the spectroscopic ellipsometer to take into account possible absorption effects in the fitting model. To fit the experimental data, a J.A. Woollam software was used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

direct patterning, femtosecond laser micromachining, hybrid polymers, photonics devices, refractive index enhancement, ultrafast nonlinear phenomena

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