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Article

Comparison of *in Situ* and *ex Situ* Methods for Synthesis of Two-Photon Polymerization Polymer Nanocomposites

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Abstract: This article reports about nanocomposites, which refractive index is tuned by adding TiO_2 nanoparticles. We compare *in situ*/*ex situ* preparation of nanocomposites. Preparation procedure is described, properties of nanocomposites are compared, and especially we examine the applicability of two-photon polymerization (2PP) of synthesized nanocomposites. All prepared samples exhibit suitable optical transparency at specific laser wavelengths. Three-dimensional structures were generated by means of two-photon polymerization effect induced by a femtosecond laser.

Keywords: high refractive index; polymer/TiO_2 nanocomposites; two-photon polymerization (2PP); 3-dimensional (3D) structures

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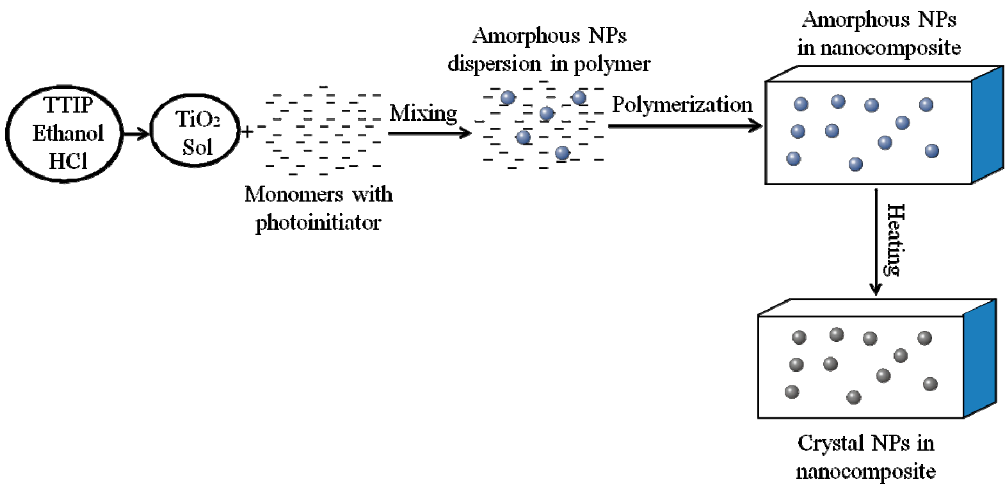
1. Introduction

Recently, the need for optical materials with high refractive index in the fields of ophthalmic lenses, filters, optical adhesives, highly reflective and antireflection coatings, as well as advanced optoelectric fabrications, are increasing [1–8]. High refractive index nanoparticles can be embedded into polymer matrix to tune the refractive index of nanocomposites. For example, PbS nanoparticles have been incorporated into gelation or poly(ethylene oxide) in order to study how the nanoparticles affect the overall refractive index of nanocomposites [9,10]. The preparation of poly(aryl ether sulfone)-based composites containing SiO_2–TiO_2–ZrO_2 has also been reported [11]. Trialkoxysilane-capped PMMA–TiO_2 hybrid thin films with high refractive index were prepared using *in situ* sol-gel method [12]. Photosensitive nanocomposites can be synthesized by adding TiO_2 nanoparticles. In comparision with common photoresists these materials have been applied to fabricate microstructures by two-photon polymerization (2PP) [13–16]. 2PP processing is a polymerization process initiated by two-photon absorption (2PA). Using 2PP technology arbitrary 3D structures can be produced. The generated structures with high refractive index can be used, e.g., in optical tweezers, as the acting forces depend on the refractive index of materials [17–19]. In [13], 2PP fabrication of three-dimensional (3D) structures by means of 2PP was demonstrated in polymers with TiO_2 nanoparticles. Firstly, the researcher wrote the 2PP structure in the polymer, and then produced the nanoparticles in the polymer matrix. Furthermore, Sakallari fabricated 2PP structures with refractive index 1.54 [16]. We compare two different strategies of generation of 2PP structures in high refractive index nanocomposites: This article reports *in situ* and *ex situ* preparation of high refractive index polymer/TiO_2 nanocomposites and analysis of structurability by 2PP when increasing the TiO_2 nanoparticles concentration. We show that the refractive index of the synthesized nanocomposites increases with the TiO_2 nanoparticle concentration dispersed in the polymer. The prepared samples exhibit suitable optical transparency at 2PP wavelength. 3D structures of nanocomposites have been produced by 2PP.

2. Experimental Section

2.1. In Situ Preparation of Nanocomposites

Figure 1. Schematic of *in situ* synthesis of nanoparticles in a polymer matrix.



In situ synthesis of nanoparticles in a polymer matrix is a simple and effective route to prepare nanocomposites. This method allows one-step fabrication of nanocomposites with *in situ* generated nanoparticles from corresponding precursors. In this case, the nanoparticles can be grown inside the polymer matrix. The advantage of this route is that it prevents particle agglomeration while maintaining a good spatial distribution in the polymer matrix. The drawback of this method is that the unreacted educts of the *in situ* reaction might influence the properties of the final material. First of all, in this article we used *in situ* method to prepare the polymer/TiO_2 nanocomposites, which is shown in Figure 1.

2.1.1. Synthesis of TiO_2 Nanoparticles

The TiO_2 nanoparticles used for in-situ preparation were synthesized in the laboratory using the sol-gel method [20–23]. Titanium (IV) isopropoxide (TTIP, 97.0%, Sigma Aldrich, St. Louis, MI, USA) was used as starting for synthesizing nanoparticles. The TiO_2 nanoparticles were synthesized by hydrolysis of TTIP in water, which was formed by decomposition of ethanol. (1) A volume of 30 mL of TTIP was mixed with 100 mL of absolute ethanol. Ethanol is a useful solvent not only to disperse TTIP, but also for hydrolysis of TTIP. The mixture was vigorously stirred at room temperature. (2) A volume of 2.7 mL of hydrochloric acid (HCl, 37.0%) was used as a catalyst for alkoxide hydrolysis, and dropped into the solution. Resultant solution was stirred used a magnetical stirrer for 30 min, subsequently bath-sonicated another 30 min, the as-synthesized TiO_2 sol is optically clear. (3) This sol-gel process is easily dried at room temperature to obtain TiO_2 nanoparticles, TiO_2 is prepared by hydrolysis of TTIP and condensation of titanium hydroxide. Scanning electron microscope (SEM) and Transmission electron microscope (TEM) have been used to characterize the size of particles and dispersion in the polymer matrix, X-ray diffraction (XRD) was used to analyze the synthesized TiO_2 nanoparticles.

2.1.2. Preparation of Photosensitive Nanocomposites Using TiO_2 Sol

This TiO_2 sol was used without further purification. TiO_2 sol was added into 4 g polymer hybrid (Ormocers-Ormocore® b59 with 1.8% Photoinitiator Irgacure from Microresist technology GmbH (Berlin, Germany), the refractive index n = 1.554 after polymerized was measured by Abbe Refractometer (OP P/2, Carl Zeiss AG, Oberkochen, Germany) at a wavelength λ = 589 nm) to prepare the polymer/TiO_2 sol nanocomposites with a concentration from 1.0 to 20.0 wt %. In addition, each TiO_2 sol in this range was dried and the solvent was completely evaporated on the hotplate. TiO_2 nanoparticles concentration in polymer was calculated with the linear fitting [15]:

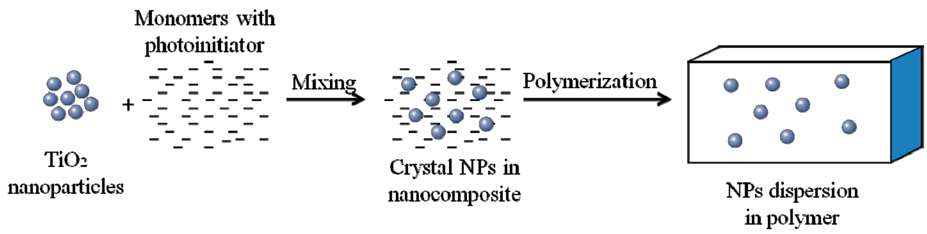
$$y \approx 0.16x \quad (1)$$

with x is TiO_2 sol weight, and y is pure TiO_2 nanoparticles after the solvent was completely dried. According to Equation (1) the concentration of pure nanoparticles is from 0.16 to 3.20 wt %. The amorphous TiO_2 nanoparticles in solution can be easily dispersed in polymer and incorporated into polymer matrix by magnetical stirrer at 90 °C to evaporate the residual solvents and sonication-bath. After the composites have been achieved, the samples will be prepared for X-ray diffraction (XRD) (Philips XRD X–pert IMS, PANalytical, Almelo, Netherlands) analysis and scanning electron microscope (SEM) (LEO 1530 Gemini FESEM, Carl Zeiss AG, Oberkochen, Germany) characterization. Refractive index was measured on an Abbe Refractometer at the wavelength of 589 nm and optical transparency was measured by UV-Vis-NIR spectrometer (Pekin Jasco V-670, Jasco Analytical instruments, Easton, PA, USA).

2.2. Ex Situ Preparation of Nanocomposites

Another important route for the preparation of polymer/TiO_2 nanocomposites is to disperse pre-made nanoparticles directly into polymer to form composites. This approach is defined as the *ex situ* synthesis of nanocomposites (Figure 2). The *ex situ* synthesis method is more suitable for large-scale industrial applications than the *in situ* method. The key challenge for this method is to be able to prepare nanoparticles, which possess higher dispersibility in the polymer and have long-term stability against aggregation. In order to solve these problems sonication methods were used to disperse the nanoparticles in the polymer.

Figure 2. *Ex situ* synthesis schemes for the preparation of nanocomposites.



Preparation of High Refractive Index Polymer/TiO_2 Nanocomposites

TiO_2 nanoparticles with refractive index $n \approx 2.43–2.8$ [24] and diameter 20 nm were used (99.5% TiO_2 with 80.0 wt % Rutile and 20.0 wt % Anatase from Evonik Degussa GmbH, Hanau, Germany) and dispersed into polymer matrix to adapt the composite's refractive index. In contrast to the TiO_2 nanoparticles used for *in situ* preparation, which were synthesized in the laboratory, the TiO_2 nanoparticles used for *ex situ* preparation were purchased from a commercial supplier. Polymer/TiO_2 composites with a concentration range between 0.001 and 3.0 wt % were prepared.

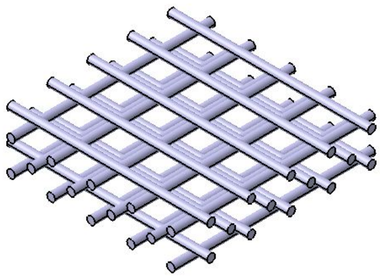
In this process the dispersion of the nanoparticles in polymer matrix becomes one critical issue in the successful preparation of these transparent hybrid nanocomposites. Particles agglomeration can significantly reduce the transparency of nanocomposite. In order to disperse the nanoparticles homogeneously in the polymer, the mixtures were first tip-sonicated for 8 min at room temperature, and subsequently the mixtures were sonicated again using a bath-type sonicator for 15 min at 20 °C.

2.3. 2PP of Nanocomposites

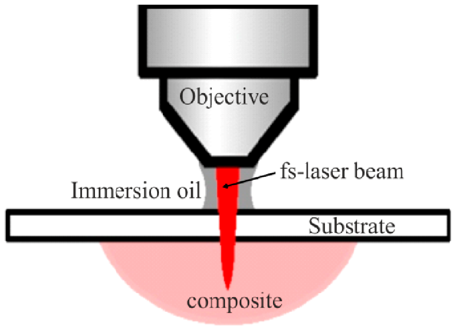
The 2PP process is initiated inside the composite by focusing a fesmtosecond laser beam into the photosensitive materials. By moving the laser focal point, arbitrary 3D structures can be directly written into the photosensitive materials. In the present work 2PP technology was used for photopolymerization of synthesized nanocomposite. In order to evaporate the residual solvent, before writing the structures, the liquid composite on the cover glass was pre-baked on the hotplate at 90 °C for 0.5 h.

We used a mode-locked frequency-doubled ytterbium-doped glass laser system at a wavelength of 515 nm with a pulse width of 240 fs as light source and a 100× oil immersion microscope objective lens (Plan Apochromat, N.A. = 1.4, Carl Zeiss AG, Oberkochen, Germany) was used to focus the laser beam into the composite (Figure 3). After polymerization, SEM was used to record images of fabricated 3D structures.

Figure 3. (**a**) Schematic of the fabricated 3D structure, a woodpile; and (**b**) Femtosecond laser fabrication principle of 3D structures.



(**a**)



(**b**)

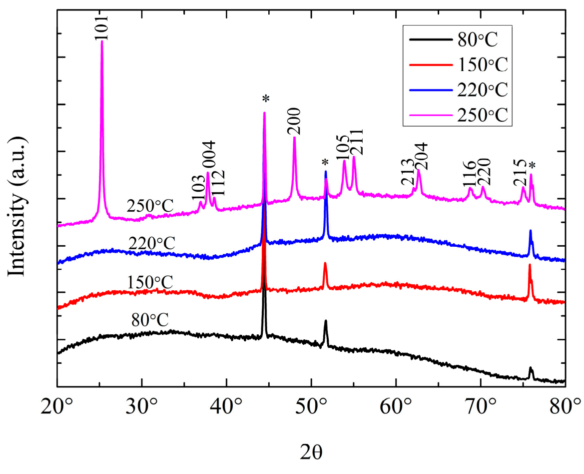
3. Results and Discussion

3.1. In Situ Process

3.1.1. X-ray Diffraction (XRD) Analysis

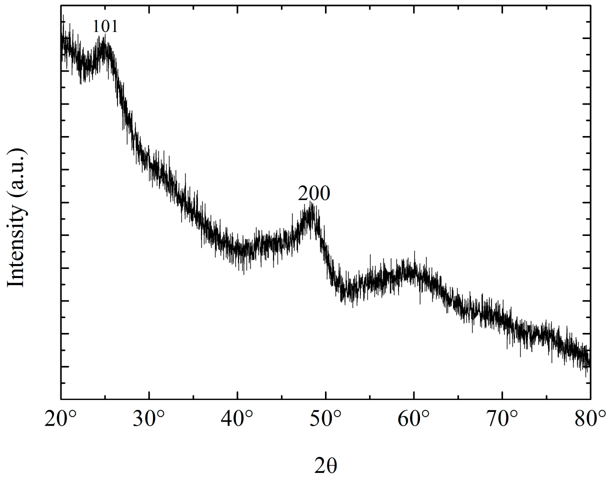
At room temperature XRD curves exhibit that TiO_2 nanoparticles have amorphous structure [15]. The refractive index of crystalline nanoparticles is higher than that of amorphous [15,24]. In order to obtain the TiO_2 crystals, we investigated the nanoparticles at different temperature. XRD patterns of heat-treated TiO_2 at different temperature are shown in Figure 4. It was observed that annealing at 250 °C leads to the formation of the anatase phase. XRD curves exhibit strong reflection peaks in the 2θ region of 20°–80° after treated at 250 °C. The identical peaks could be assigned to originate from reflection by (101), (103), (004), (112), (200), (105), (211), (213), (204), (116), (220), and (215) planes of TiO_2 anatase crystals, matching well with its simulated anatase crystal structure [25].

Figure 4. XRD patterns of pure TiO_2 nanoparticles heat-treated at 80 °C, 150 °C, 220 °C, and 250 °C was obtained by using CuKα radiation at λ = 1.5406 µm, (*) shows substrate Incubo peak.



We investigated the polymerized nanocomposites after heat-treated for 24 h at 250 °C, the reflection peaks (101) and (200) in Figure 5 were matched with standard anatase crystal. It can be confirmed that the TiO_2-anatase crystal after heat-treated at 250 °C in vacuum oven can be obtained in the composites.

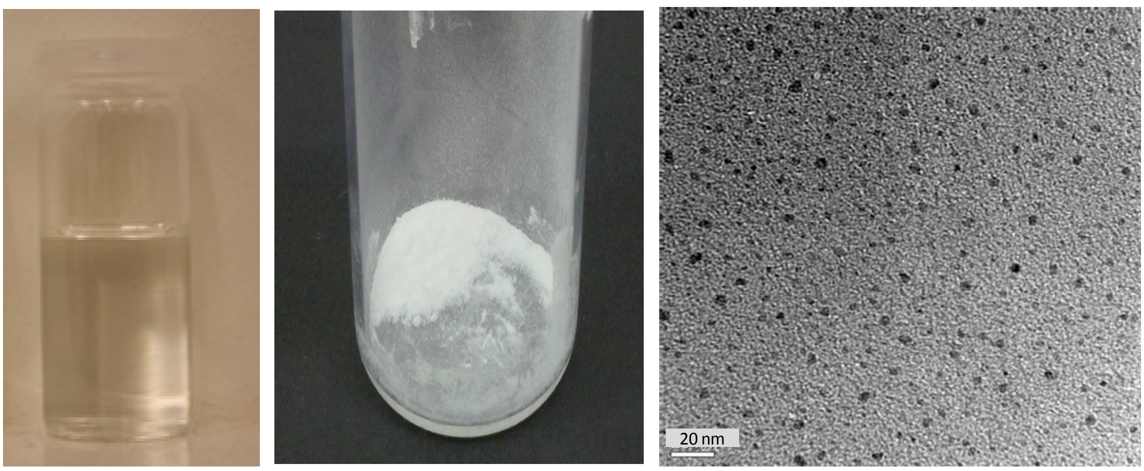
Figure 5. XRD-pattern of nanocomposite with 0.16 wt % TiO_2 heat-treated at 250 °C.



3.1.2. TEM/SEM Characterization

TiO_2 nanoparticles synthesized using the *in situ* method as described in Section 2.1.1 was characterized by Transmission Electron Microscopy (TEM) (CM200, Philips, Eindhoven, Netherlands). The TiO_2 sol was transparent, and the nanoparticles were dispersed in the sol (Figure 6a). Figure 6b shows the nanoparticles after the sol was completely dried. Figure 6c shows the TEM image of the TiO_2 nanoparticles after the sol was completely dried. The average particle size of the TiO_2 nanoparticles observed from TEM analysis was approximately 5 nm.

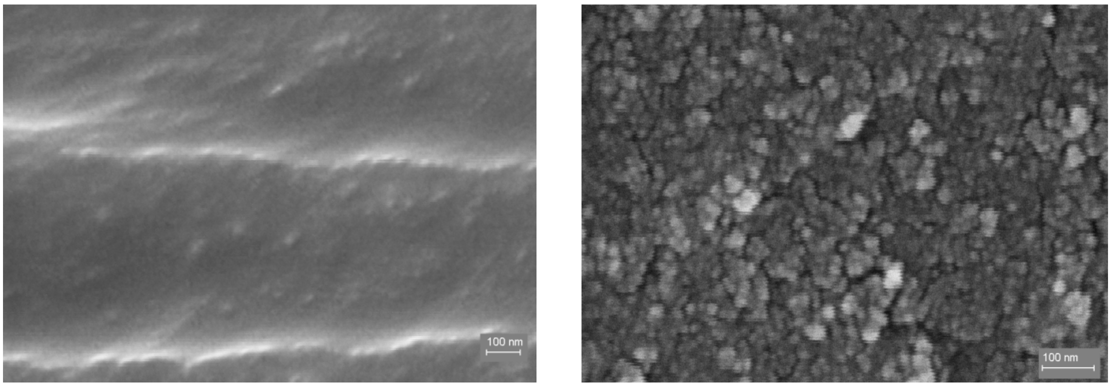
Figure 6. (**a**) Synthesized TiO_2 sol and (**b**) TiO_2 nanoparticles after drying and (**c**) TEM image of dried TiO_2 nanoparticles.



(**a**) (**b**) (**c**)

After the TiO_2 particles in sol were incorporated directly into the polymer matrix at different concentrations, the resulting composites were polymerized under a UV lamp. The SEM images of samples at 0.16 and 0.64 wt % TiO_2 nanoparticles at cross-section are shown in Figure 7.

Figure 7. SEM of polymerized nanocomposites from cross section at various TiO_2 nanoparticle concentrations: (**a**) 0.16 wt % and (**b**) 0.64 wt %.

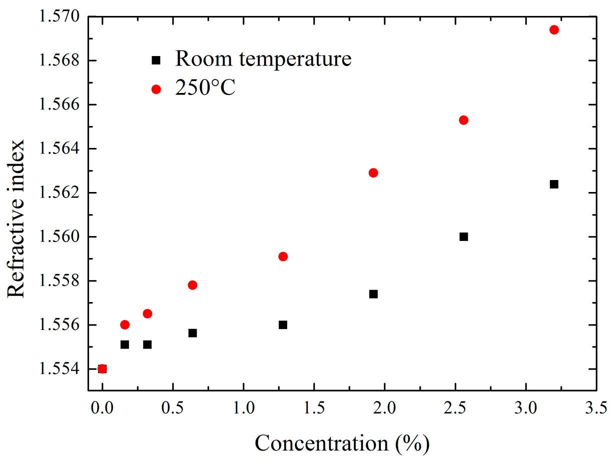


(**a**) (**b**)

3.1.3. Refractive Index Measurements

The refractive index of synthesized nanocomposites can be modified by changing the nanoparticles concentration. Figure 8 shows the variation of refractive index both at room temperature, as well as after heat-treated at 250 °C. First of all, the samples were prepared directly after the residual solvent was evaporated at 90 °C on a magnetic stirrer, as in the beginning the TiO_2 sol was mixed with polymer, there are other lower refractive index solvents in the mixture, such as H_2O (n = 1.33) and ethanol (n = 1.36), respectively.

Figure 8. Variation of refractive index at room temperature and after heat-treated at 250 °C in an oven heat-treated 2 h TiO_2 nanoparticles. The accuracy of the refractive index determination is limited by the measuring device to approximately 0.0005.



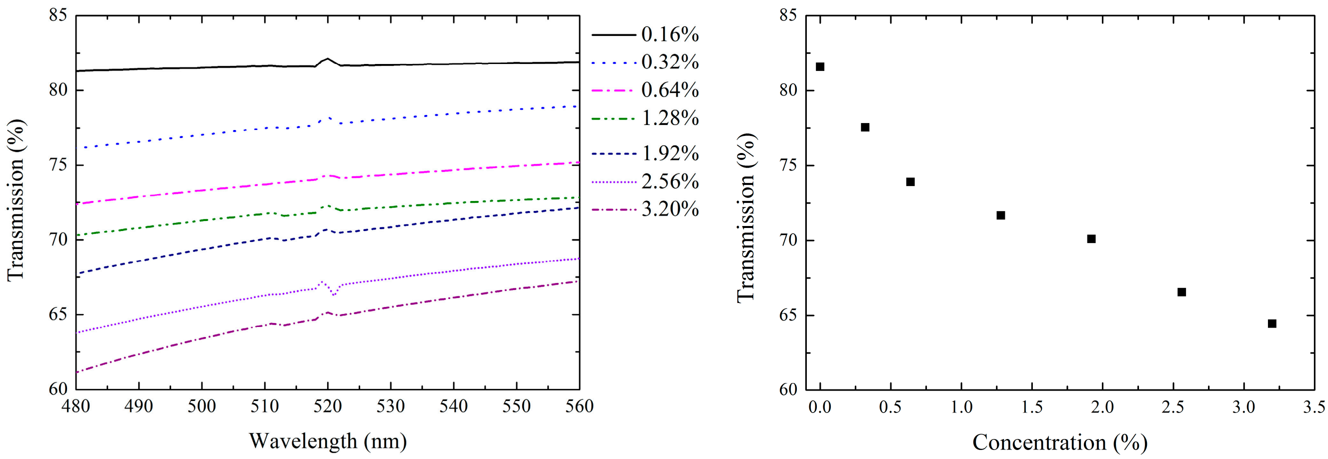
Then, the polymerized samples with thickness of thin film 300 μm were measured using Abbe Refractometer (Figure 8). Furthermore, the polymerized samples were heat-treated in an oven at

250 °C for 2 h in order to obtain the TiO_2 crystals, as the refractive index of TiO_2 crystals is higher than that of amorphous TiO_2 nanoparticles. Figure 8 shows the refractive index is increasing by increasing the concentration, after 250 °C heat-treated the refractive index of polymerized samples is higher than at room temperature.

3.1.4. Optical Characterization

In this article a method for the fabrication of 3D submicrostructures doped with TiO_2 nanoparticles based on 2PP is presented. For 2PP processing, high transparency at the used wavelength (515 nm) is required to efficiently localize the focal point of the laser. Therefore the optical properties have to be measured and adapted. The transmission of synthesized composites was investigated and measured by using UV-Vis-NIR spectrometer, as the nanocomposites have higher transmission, the laser beam can be transmitted through the composite to write 3D structures. Figure 9a displays the transmission spectra of nanocomposite in the 480–560 nm area; Figure 9b shows the transmission at 2PP wavelength 515 nm. It is clearly that the transmission with 0.16–3.20 wt % of TiO_2 nanoparticles is above 60%, and can potentially be used for 2PP structuring. It has been also shown that increasing TiO_2 nanoparticle concentration indicates decreasing transmission.

Figure 9. (**a**) Transmission spectra of the composite in the wavelength 480–560 nm; and (**b**) Additionally the transmission at 2PP processing wavelength 515 nm with different TiO_2 nanoparticle concentrations.

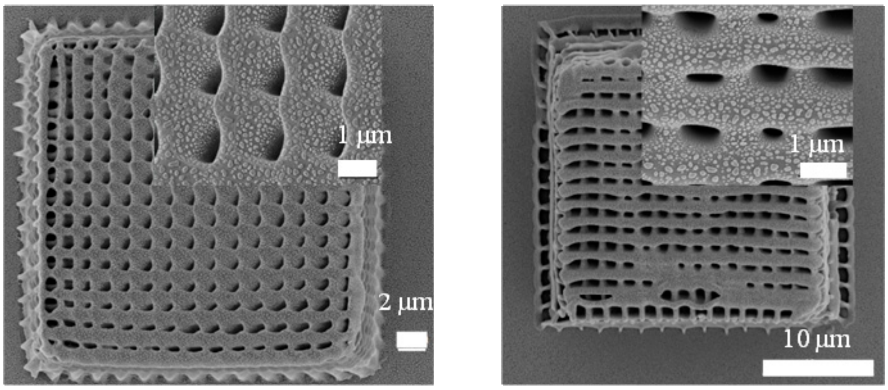


(**a**) (**b**)

3.1.5. 2PP Results

For demonstration of 3D structure fabrication, the woodpile structure was chosen. The 3D structures both at low (0.16 wt % TiO_2 nanoparticles) and high (2.56 wt % TiO_2 nanoparticles) concentrations are generated with a writing speed of 2.0 mm/s and with a laser power of 1.4 mW [15]. The resulting 2PP-fabricated structures contain amorphous TiO_2 nanoparticles, which were demonstrated by XRD analysis. The samples used in [15] were not heat treated. However, the refractive index of amorphous TiO_2 is lower than that for crystalline TiO_2. Therefore, samples in this study were thermally treated at 250 °C for 2 h. In Figure 10, nanoparticles on the surface of structures were observed. These nanoparticles are TiO_2 anatase, which was generated through reaction between Ti^{4+} ions and H_2O, can be confirmed by XRD. This result is clear evidence that using 2PP processing we have successfully generated the structures containing the nanoparticles in the polymer matrix.

Figure 10. SEM images of structures of in-situ prepared polymer/nanoparticles composites produced by 2PP after thermal treatment for 2 h at 250 °C at (**a**) 0.16 wt % and (**b**) 2.56 wt % TiO_2 sol. Insets (upper right) confirm that nanoparticles are on surface.



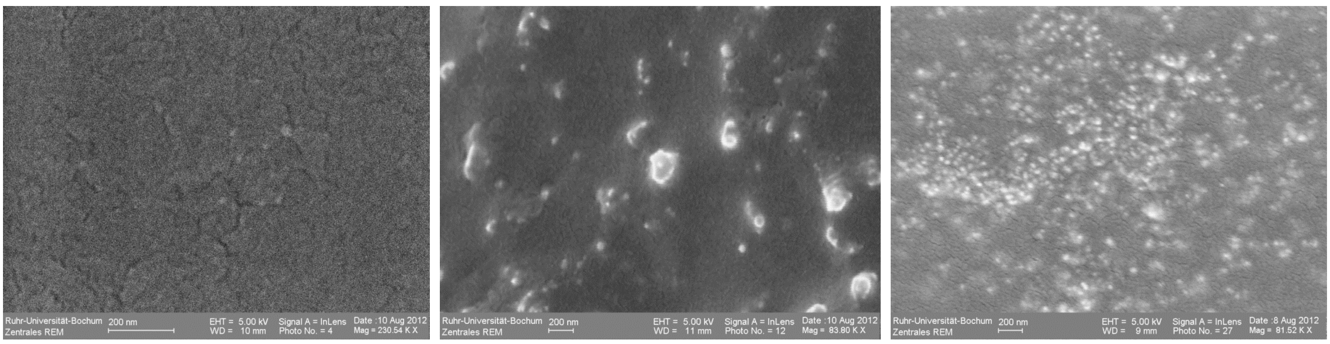
(**a**) (**b**)

3.2. Ex Situ Process

3.2.1. SEM Characterization

Figure 11 shows SEM images of nanoparticles dispersion at different concentrations: 0.001 (a), 0.1 (b) and 2.0 wt % (c). The nanoparticles are highly dispersed in polymer, the higher the concentration, the more the nanoparticles in polymer, and the nanoparticles were agglomerated; In this case it will be influenced on measurements in transmission and refractive index. Using 2PP processing to write structures, the laser beam will be scattered by agglomerated nanoaprticles at high concentration, which will distort the fabricated structures.

Figure 11. Nanoparticles dispersion at concentration (**a**) 0.001 wt %, (**b**) 0.1 wt % and (**c**) 2.0 wt %.

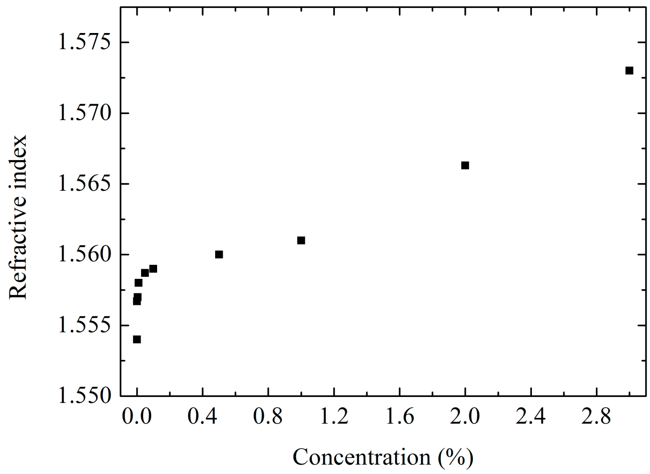


(**a**) (**b**) (**c**)

3.2.2. Refractive Index Measurements

The refractive index can be modified by changing the TiO_2 concentration, as shown in Figure 12. The refractive index was measured by 8 min tip-sonication using an Abbe Refractometer. The refractive index increased with increasing TiO_2 composite concentration, indicating that doping concentration is an important factor. The increase in refractive index clearly exceeded the precision of the refractive index measuring device (approximately 0.0025).

Figure 12. Refractive index results at different TiO_2 composite concentrations and 8 min tip-sonication.

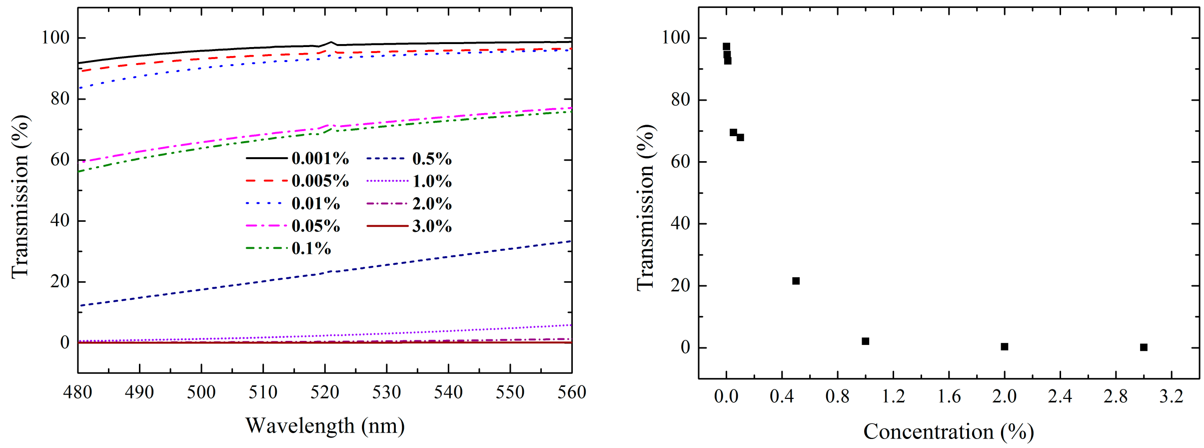


3.2.3. Optical Characterization

The transmission of synthesized composites was investigated and measured by using UV-Vis-NIR spectroscopy.

Figure 13a displays the transmission spectra of nanocomposite in the 480–560 nm area; Figure 13b shows the transmission at 2PP wavelength 515 nm. It is clearly that the transmission with 0.001–0.1 wt % of TiO_2 nanoparticles is above 60%, which indicates higher optical transparency, and can potentially be used by means of 2PP to write structures. It has been also shown that increasing concentration indicates decreasing transmission. The transmission with 0.5–3.0 wt % of TiO_2 nanoparticles is below 60%, the laser beam is difficult to transmit through the composite, therefore the laser beam will be strongly scattered by nanoparticles, which 3D structures cannot easily fabricate.

Figure 13. (**a**) Transmission spectra of various composite concentrations in the wavelength range of 480–560 nm; and (**b**) Transmission of composite concentrations at 2PP processing wavelength of 515 nm; Tip-sonication time for all samples was 8 min.

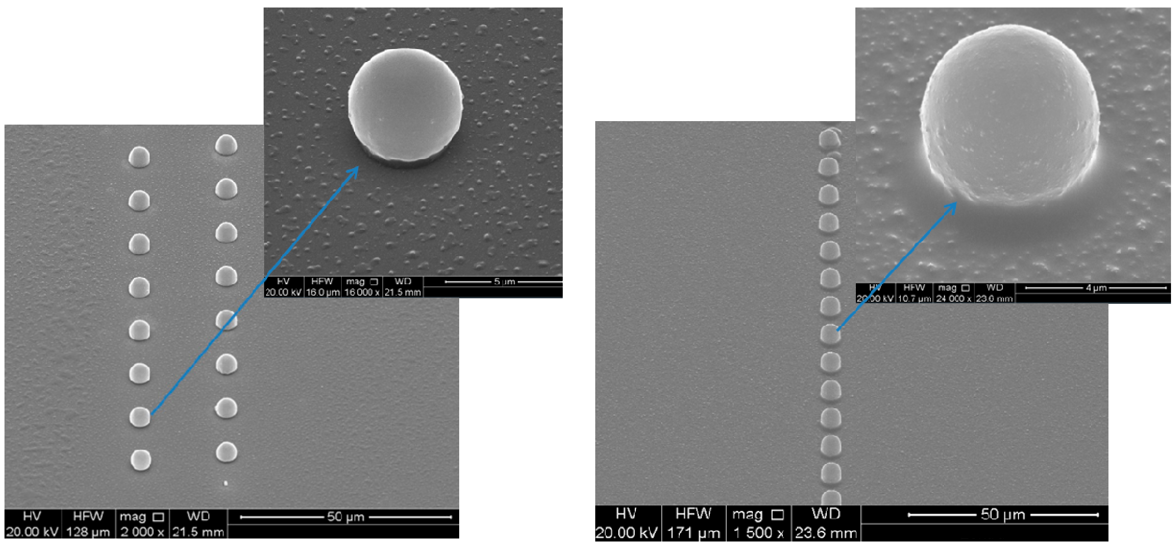


(**a**) (**b**)

3.2.4. 2PP Results

Figure 14 shows the fabricated 3D structures by 2PP processing at 0.001 wt % (Figure 14a) and 0.5 wt % (Figure 14b). The inset of upper right structure (Figure 14a) is fabricated at laser power 10 mW and writing speed 1 mm/s, compared to the inset of upper right (Figure 14b) at laser processing power 7 mW and writing speed 1 mm/s. It can be clearly seen that, at low concentrations, the structure is smoother than at high concentrations; after the structures were fabricated, both of the structures and the surface of substrate were washed cleanly. At a concentration of 0.5 wt % the transparency is even below 20%, however, we have successfully fabricated the structures. We have tried to write the structures at higher concentrations than 1.0 wt %, the structures were heavily distorted depending on the low transparency, at which the laser beam could not transmit through the nanocomposite.

Figure 14. SEM images of 2PP *ex situ* prepared structures at (**a**) 0.001 wt % with $P = 10$ mW, $v = 1$ mm/s and (**b**) 0.5 wt % with $P = 7$ mW, $v = 1$ mm/s.



(**a**) (**b**)

4. Conclusions

We have presented the results from investigations into high refractive index polymer/TiO_2 nanocomposites, which can be successfully structured by 2PP. In the *in situ* process: We have synthesized high refractive index nanocomposites. All samples exhibit suitable optical transparency at the 2PP wavelength, in which the laser beam can transmit through the nanocomposite to write arbitrary 3D structures. In the beginning, the refractive index of synthesized nanocomposites is not too high, e.g., the refractive index at 2.0 wt % was approximately 1.557. After heat-treatment, the refractive index significantly increased, *i.e.*, the refractive index at 2.0 wt % was approximately 1.563. The heat treatment process generated TiO_2 anatase nanoparticles. In the *ex situ* process: sonication-tip was used to disperse the nanoparticles in the polymer. High refractive index nanocomposites have been directly synthesized, e.g., the refractive index at 2.0 wt % is about 1.565. Although this is higher than the refractive index obtained by the *in situ* procedure, it is not possible to write structures using lasers when the *in situ* procedure is used; this should be considered when choosing between the *in situ* and *ex situ* methods of polymer composite preparation for a particular application. The refractive index of both *in situ* and *ex situ* prepared nanocomposites can be tuned by increasing the TiO_2 concentration. However, at higher concentrations, the optical transparency becomes unsuitable for the 2PP wavelength of 515 nm. In such a case, the laser beam scatters, and, as a result, cannot transmit through the nanocomposite to write 3D structures. The prepared samples exhibit suitable optical transparency for 2PP processing. Using 2PP technology, structures with high refractive index have also been produced. In this way, the synthesized composites can be used both as high refractive index and as structural polymers.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Cui, Z.; Lü, C.; Yang, B.; Shen, J.; Yang, H. The research on syntheses and properties of novel epoxy/polymercaptan curing optical resins with high refractive indices. *Polymer* **2001**, *42*, 10095–10100.
2. Okutsu, R.; Ando, S.; Ueda, M. Sulfur-containing poly(meth)acrylates with high refractive indices and high Abbe's numbers. *Chem. Mater.* **2008**, *20*, 4017–4023.
3. Nebioglu, A.; Leon, J.A.; Khudyakov, I.V. New UV-curable high refractive index oligomers. *Ind. Eng. Chem. Res.* **2008**, *47*, 2155–2159.
4. Hart, S.D.; Maskaly, G.R.; Temelkuran, B.; Prideaux, P.H.; Joannopoulos, J.D.; Fink, Y. External reflection from omnidirectional dielectric mirror fibers. *Science* **2002**, *296*, 510–513.

5. Dobrowolski, J.A.; Ho, F. High performance step-down AR coating for high refractive–index IR materials. *Appl. Opt.* **1982**, *21*, 288–292.
6. Yablonovitch, E. How to be truly photonic. *Science* **2000**, *289*, 557–559.
7. Hornak, L.A. *Polymers for Lightwave and Integrated Optics: Technology and Applications*; Marcel Dekker, Inc.: New York, NY, USA, 1992.
8. Kitai, A.H. *Solid State Luminescence*; Chapman & Hall: London, UK, 1993.
9. Zimmermann, L.; Weibel, M.; Caseri, W.; Suter, U.W. High refractive index films of polymer nanocomposites. *J. Mater. Res.* **1993**, *8*, 1742–1748.
10. Kyprianidou-Leodidou, T.; Caseri, W.; Suter, U.W. Size variation of PbS particles in high-refractive-index nanocomposites. *J. Phys. Chem.* **1994**, *98*, 8992–8997.
11. Wang, B.; Wilkes, G.L. High Refractive-Index Ceramic/Polymer Hybrid Material. U.S. Patent 5,109,080, 13 July 1992.
12. Lee, L.H.; Chen, W.C. High-refractive-index thin films prepared from trialkoxysilane-capped poly(methyl methacrylate)-tiania materials. *Chem. Mater.* **2001**, *13*, 1137–1142.
13. Duan, X.M.; Sun, H.B.; Kaneko, K.; Kawata, S. Two-photon polymerization of metal ions doped acrylate monomers and oligomers for three-dimensional structure fabrication. *Thin Solid Films* **2004**, *453*, 518–521.
14. Ostendorf, A.; Chakif, M.; Guo, Q. Laser direct writing of nanocompounds. In Proceedings of Materials Research Society Spring Meeting and Exhibits, San Francisco, CA, USA, 26–29 April 2011.
15. Guo, Q.; Ghadiri, R.; Xiao, S.; Esen, C.; Medenbach, O.; Ostendorf, A. Laser direct writing of high refractive index polymer/TiO_2 nanocomposites. In Proceedings of SPIE Photonics West, San Francisco, CA, USA, 21 January 2012.
16. Sakellari, I.; Gaidukeviciute, A.; Giakoumaki, A.; Gray, D.; Fotakis, D.; Farsari, M.; Vamvakaki, M.; Reihardt, C.; Ovsianikov, A.; Chichkov, B.N. Two-photon polymerization of titanium-containing sol-gel composites for three-dimensional structure fabrication. *Appl. Phys. A* **2010**, *100*, 359–364.
17. Ashkin, A.; Dziedzic, J.M.; Bjorkholm, J.E.; Chu, S. Observation of a single-beam gradient force optical trap for dielectric particles. *Opt. Lett.* **1986**. 11, 288–290.
18. Kelemenen, L.; Valkai, S.; Ormos, P. Integrated optical motor. *Appl. Opt.* **2006**, *45*, 2777–2780.
19. Harada, T.; Yoshikawa, K. Mode switching of an optical motor. *Appl. Phys. Lett.* **2002**, *81*, 4850–4852.
20. Jean, J.H.; Ring, T.A. Nucleation and growth of monosized TiO_2 powders from alcohol solution. *Langmuir* **1986**, *2*, 251–255.
21. Kim, T.H.; Lim, D.Y.; Yu, B.S.; Lee, J.H.; Goto, M. Effect of stirring and heating rate on the formation of TiO_2 powders using supercritical fluid. *Ind. Eng. Chem. Res.* **2000**, *39*, 4702–4706.
22. Hirai, T.; Sato, H.; Komasawa, I. Mechanism of formation of titanium dioxide ultrafine particles in reverse micelles by hydrolysis of titanium tetrabutoxide. *Ind. Eng. Chem. Res.* **1993**, *32*, 3014–3019.
23. Wu, C.I.; Huang, J.W.; Wen, Y.L.; Wen, S.B.; Shen, Y.H.; Yeh, M.Y. Preparation of TiO_2 nanoparticles by supercritical carbon dioxide. *Mater. Lett.* **2008**, *62*, 1923–1926.
24. Lide, D.R. *Handbook of Chemistry and Physics*, 76th ed; CRC Press: Boca Raton, FL, USA, 1995.

25. Hu, M.Z.-C.; Kurian, V.; Payzant. E.A.; Rawn, C.J.; Hunt, R.D. Wet-chemical synthesis of monodispersed barium titanate particles—Hydrothermal conversion of TiO_2 microspheres to nanocrystalline $BaTiO_3$. *Powder Technol.* **2000**, *110*, 2–14.

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