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Refractive Index Border Associated with Nonlinear Optical Properties in Superhybrid Transparent TiO₂ Nanoparticles-Polymer: Great Potential for Ultrafast Optical Waveguide in Optical Communication

Hendry Izaac Elim,^{1-7*}

¹Nanomaterials for Photonics Nanotechnology Laboratory (**N4PN Lab.**), Department of Physics, Faculty of Mathematics and Natural Sciences (**FMIPA**), Pattimura University (**UNPATTI**), Jl. Ir. M. Putuhena, Poka, Ambon, Indonesia 97233

²Nanotechnology Research Center and Innovative Creation (**PPNRI-LPPM**), and Nanomedicine Garden in Research and Society Center of Pattimura University, **UNPATTI**, Jl. Mr. CHR. Soplanit, Rumah Tiga, Ambon, Indonesia 97234

³Multidisciplinary Bioinformatics Laboratory (**MB Lab.**), Biology Department, **UNPATTI**, Jl. Ir. Martinus Putuhena, Poka, Ambon, Indonesia 97233

⁴Theoretical Physics Laboratory (**TP Lab.**), Department of Physics, **FMIPA**, **UNPATTI**, Jl. Ir. M. Putuhena, Poka, Ambon, Indonesia 97233

⁵Specific Laboratory of Electronics and Instrumentation, Physics Department, Pattimura University, Ambon, Maluku, Indonesia 97233

⁶Ambon Academy of Science and Arts (**A-ASA**), Kapitan Permata Street, Ambon Island, Indonesia 97582.

⁷Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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Corresponding author: *Email: : hendryelim@gmail.com; hendry.elim@staff.unpatti.ac.id

Abstract

The excellency of a superhybrid material based TiO₂ nanoparticles (NPs) has been improved by the surface modification of the TiO₂ with a coupling agent of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane to render them highly compatible with organic monomer mixtures avoiding aggregation. Such TiO₂ NPs are then attached with a polymer. The border of linear refractive index of hybrid TiO₂ NPs-polymer is enhanced in comparison with that of pure epoxy resin or polymer. Nonlinear refractive index and nonlinear absorption coefficient of hybrid TiO₂ NPs-polymer are measured by femtosecond Z-scan technique at 800 nm. This hybrid material has been fabricated and studied to have a great potential for ultrafast optical waveguide in optical communication quantified by the propagation loss of the hybrid TiO₂ NPs-polymer optical waveguide in the range of 4.79 to 11.90 dB/cm, which is depending on the volume percent of TiO₂ NPs.

Keywords: Superhybrid material, TiO₂ nanoparticle, Waveguide, Optical property.

The invented contribution: A simple process to improve superhybrid materials with an excellence optical behavior for future waveguide device.

ARTICLES

I. INTRODUCTION

Superhybrid materials based on organic-inorganic hybrid materials are considered to be promising materials that may exhibit novel optical, ultrafast nonlinear optical, mechanical, electronics, magnetic, photovoltaic, and conductivity [1-11]. In particular, polymer-inorganic nanohybrid materials with high refractive index and transparency play important role in the fields of

optical waveguides and switching, ophthalmic lenses, antireflection coatings, and adhesives for optical and electronics components. To overcome the limitation of refractive index in polymer materials, it is necessary to combine the organic materials with high refractive index inorganic nanoparticles (NPs), such as TiO₂, CdS, ZrS, ZrO₂, SnO₂, and PbS [12-16].

Among the numerous materials being researched, TiO₂ NPs are a suitable inorganic component for increasing the refractive index of the hybrid organic-nanocomposites. This is because TiO₂ NPs have a high refractive index ($n \sim 2.5$ and 2.7 , in the crystal forms of anatase and rutile, respectively). However, the optical

scattering of inorganic NPs, responsible for opacity, must be avoided for these hybrid materials. Therefore, it is important to choose small particles with diameters below one-tenth of the wavelength of visible light (400–790 nm) (typically < 25 nm) so that this can avoid Rayleigh scattering [17-19] and can be incorporated into a transparent polymer matrix to fabricate high refractive and large nonlinear optical films of hybrid polymer-nanocomposites.

In present work, we modified the surface of TiO₂ using coupling agent of 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane and then dispersed them into the polymer matrices without aggregation. We chose monomer of 2,2-Bis(4-glycidyloxyphenyl)-propane (DGEBA) blended with phthalic anhydride (C₈H₄O₃) in γ -butyrolactone solvent. This prepolymer exhibits a high refractive index, good solvent-resistance, good thermal stability, and good mechanical strength. Furthermore, we report our investigation into linear refractive index and nonlinear optical properties in a series of thin films of transparent hybrid TiO₂ NPs-polymer. Our results show that such hybrid materials possess very high linear refractive index and large optical nonlinearity, and have a great potential for optical waveguide and optical communication.

II. EXPERIMENTAL METHOD FOR SAMPLE PREPARATION

The samples of hybrid TiO₂ NPs-polymer were prepared with three steps. The first step is by modifying the surface of TiO₂ NPs with 2-(3,4-epoxycyclohexyl)

ethyltrimethoxysilane. In this step, each weight of TiO₂ NPs was diluted in 250 ml methanol and sonicated for 20 minutes with high power ultrasonic generator. Each solution was then mixed with 0.09 g coupling agent of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane diluted in 20 ml methanol. The mixture of these TiO₂ NPs and coupling agent solutions was then sonicated in a high-power bath sonicator for 20 minutes. To obtain a uniform compound of the structure shown in **Fig. 1**, the solution was sonicated for more than 8 hours in ultrasonic bath. The second step is a step polymerization for making a precursor. In this step, each 0.763 g monomer of 2,2-Bis(4-glycidyloxyphenyl)-propane (DGEBA) was blended with 0.33 g phthalic anhydride (C₈H₄O₃) in 2 ml γ -butyrolactone solvent. The solution was stirred for 15 hours at 120 °C in Si oil bath. The final step is to synthesize hybrid TiO₂ NPs-polymer. This step was divided by several steps of experiment as follows. First step is to evaporate 300 ml solution of the mixture between TiO₂ NPs and coupling agent to be 100 ml with 40 °C water bath. Secondly, the 100 ml solution was added with 100 ml 2-butanone and epoxy resin. Thirdly, this blended solution was sonicated for 3 hours. After sonication, the hybrid TiO₂ NPs-polymer was filtered with 1 μ m pore diameter membrane and then finally evaporated at 40 °C until the solution become 3 ml. **Table 1** shows the weight of each component used in the hybrid TiO₂ NPs-polymer. To make the thin films, part of 3 ml solution of each sample was dropped in glass substrate and spin-coated using Clean-Bench, Brand Bio-LABO with the speed of 2000 rpm for 60 seconds. **Figure 2** displays briefly the process of the fabrication of

hybrid TiO₂ NPs-polymer thin films with different volume percent of TiO₂ NPs.

Table 1. Weight of each component used in the hybrid TiO₂ nanoparticles-polymer.

TiO ₂ Nanoparticles (g)	Coupling agent (C ₁₁ H ₂₂ O ₄ Si) (g)	DGEBA (C ₂₁ H ₂₄ O ₄) (g)	Phthalic anhydride (C ₈ H ₄ O ₃) (g)	TiO ₂ Nanoparticles (Vol.%)	TiO ₂ Nanoparticles (Wt.%)
0	0.09	0.763	0.33	0	0
0.105	0.09	0.763	0.33	2.7	8
0.210	0.09	0.763	0.33	5.3	15
0.428	0.09	0.763	0.33	10	26.2
0.800	0.09	0.763	0.33	17.6	40.4
1.600	0.09	0.763	0.33	30	57.6

Figure 1. Surface modification of TiO₂ nanoparticles (NPs) with coupling agent of 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane.

Figure 2. (a) The structure of monomer of 2,2-Bis(4-glycidyloxy phenyl)-propane (DGEBA). (b) DGEBA mixed together with phthalic anhydride (C₈H₄O₃) in γ -butyrolactone solvent. (c) Hybrid TiO₂ NPs-polymer thin films with different volume percent of TiO₂ NPs.

III. RESULTS AND DISCUSSION

Figure 3(a) shows that there is an oscillation in UV-Vis spectrum of hybrid TiO₂ NPs-polymer with large content of TiO₂ NPs. This is due to light interference and scattering, which is commonly associated with guest-host structures with different refractive indices for guest and host materials. In addition, weak confinement may also contribute to the absorption below band gap energy. The exciton Bohr radius a_B in bulk TiO₂ solid is 0.8 nm if the effective masses ($m_e = 10 m_0$ and $m_h = 0.8 m_0$) are used [20]. In the NPs, the exciton energy can be estimated by using Brus formula [21]: $E_{exc} = E_g + R_y(\pi^2 a_B^2/R^2 - 3.6 a_B/R)$, where the Rydberg energy unit, $R_y = \mu e^4/2\epsilon^2 \hbar^2$, E_g ($=3.2$ eV) is the band-gap energy of anatase TiO₂ solid [20], and R is the particle radius. Two terms in the brackets represent kinetic energy and Coulomb interaction. With $R \sim 6$ nm, we find the exciton energy is 3.11 eV. This exciton energy is located at 0.02 eV below band gap of hybrid TiO₂ NPs-polymer as depicted in Fig. 3(b).

The refractive index was measured with metricon, model 2010/M prism coupler.

Figure 4 shows that the refractive index increases linearly from 1.55-1.57 to 1.75-1.82 depending on the volume percent of TiO₂ NPs and the wavelength. The refractive index of the polymer used in this study is between 1.55 and 1.57 depending on the wavelength, and the hybrid TiO₂ NPs-polymer results an increase in the refractive index of the nanocomposites films. Such a big different of refractive index between pure polymer or epoxy resin and the TiO₂ NPs indicates that hybrid TiO₂

NPs-polymer is useful for optical waveguide based on organic-inorganic hybrid materials.

Figure 3. (a) UV-Vis spectrum of transparent hybrid TiO₂ NPs-polymer with different volume percent of TiO₂. (b) The estimation of energy gap of hybrid TiO₂ NPs-polymer.

Figure 4. Refractive index as a function of volume percent in transparent hybrid TiO₂ NPs-polymer measured with different wavelengths.

The nonlinear optical measurements were carried out with the single beam z-scan technique. The laser light source is a mode-locked Ti:Sapphire of Coherent Mira Model 900-F with a high repetition rate of 76 MHz at wavelength of 800 nm, which has a temporal width of about 200 fs and a peak power of up to 50 kW. The signal profile of the laser beam was determined to be approximately Gaussian. The beam was then focused by a lens with the beam waist of 55 μm ($Z_0 = 0.12$ mm) at 800 nm. All measurements were carried out at room temperature. **Figure 5(a)** presents a typical open-aperture Z-scans of transparent hybrid TiO₂ NPs-polymer with different volume percent of TiO₂ NPs. The results show that the larger the volume percent of TiO₂ NPs is, the larger the nonlinear absorption coefficient or the imaginary part of third-order susceptibility is. In 0 Vol.% of TiO₂ NPs or a pure polymer, there is no contribution of third-order susceptibility. The largest imaginary part of third-order susceptibility, $\text{Im } \chi^{(3)}$ was obtained in hybrid TiO₂ (30 vol.%) - polymer with the value of 3.9×10^{-11} esu. Similarly, the highest nonlinear refractive index, n_2 ($= 5.0 \times 10^{-4}$ cm/GW, or $\text{Re } \chi^{(3)} = 4.1 \times 10^{-11}$ esu) is also found in the TiO₂(30 vol.%) - polymer. Therefore, the absolute value of $\chi^{(3)}$ is 5.6×10^{-11} esu. This value is about three order larger than the third-order susceptibility of colloidal TiO₂ NPs with diameter of 10 nm measured using the interface third-harmonic (TH) generation technique at wavelength of 1250 nm. Such a large different is anticipated for the following reasons: (1) the nonlinear absorption coefficient and nonlinear refractive index are enhanced by two-photon resonance at exciton band; (2) different size and volume

percent, in particular, Shcheslavskiy's result [22] was obtained from the number of TiO₂ NPs at around 10^{14} cm⁻³, in which this concentration is much lower than that in thin films; and (3) different host materials, in which the refractive index in hybrid TiO₂ NPs-polymer increases with the increase of TiO₂ NPs volume percent.

Figure 5. (a) Open- and (b) closed-aperture Z-scans of transparent hybrid TiO₂ NPs-polymer measured at the same irradiance and wavelength. (c) $\text{Im } \chi^{(3)}$ and $\text{Re } \chi^{(3)}$ as a function of volume percent of TiO₂ NPs in hybrid TiO₂ NPs-polymer.

To evaluate the intrinsic propagation loss of the hybrid TiO₂ NPs-polymer optical waveguide, we fabricate a series of the optical waveguide with different lengths and volume percent of TiO₂ NPs. The example of the waveguide is shown in **Fig. 6**. **Figure 7** shows insertion loss dependence on the waveguide length in hybrid TiO₂ NPs-polymer with different volume percent of TiO₂ NPs measured at 1320 nm. We obtain the propagation loss of the hybrid TiO₂ NPs-polymer optical waveguide in the range of 4.79 to 11.90 dB/cm, which is depending on the volume percent of TiO₂ NPs. This value is few times higher than that in the serially grafted optical waveguide of PMMA/DR1 [23]. Such high propagation loss is due to high volume percent of TiO₂ NPs. For linear and nonlinear optical applications, it is necessary to fabricate the hybrid optical waveguide with low volume percent of TiO₂ NPs.

Figure 6. (a) Hybrid TiO₂ NPs-polymer optical waveguide with the cladding of AT3925M (from NTT-AT). (b) Microscope image of the waveguide cross-section.

Figure 7. Insertion loss dependence on the waveguide length in TiO₂ NPs-polymer with different volume percent of TiO₂ NPs measured at 1320 nm. The solid line is the fitting curve of the loss.

IV. CONCLUSION

In summary, we have investigated linear refractive index and nonlinear optical properties of hybrid TiO₂ NPs-polymer and found that both linear refractive index and nonlinear index increase as the volume percent of TiO₂ NPs increases. Such high refractive index and large nonlinear indexes with low propagation loss make hybrid TiO₂ NPs-polymer a good candidate for optical waveguide and optical communication.

Conflict of interest

The authors declare no competing financial interest.

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A short CV of Corresponding author

***ORCID ID of H. I. E.:**
0000-0002-4272-7115

Assoc.Prof. H.I. Elim is a creative Indonesia physicist with the theoretical physics background particularly in his B.Sc and M.Sc. He did a scientific development of nanoscience and nanotechnology as well as nanomedicine in the last 20 years with an incredible output of ~85 high quality works published in about 34 Q1 journals according to SCOPUS/ Web of Science with h index of 25. Dr. Elim educated over 75 research students in the last 6 years as soon as the opening of nanotechnology research center and innovative creation (PPNRI) at Pattimura university on 24th April 2015.

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