Transparent nanohybrids of nanocrystalline TiO₂ in PMMA with unique nonlinear optical behavior

Akhmad Herman Yuwono,⁎a Junmin Xue,⁎a John Wang,⁎b Hendry Izaac Elim,⁎b Wei Ji,⁎b Ying Li⁎ and Timothy John Whitec

aDepartment of Materials Science, Faculty of Science, National University of Singapore, Singapore 119260. E-mail: naswangj@nus.edu.sg
bDepartment of Physics, Faculty of Science, National University of Singapore, Singapore 117542
ccentre for Advanced Research of Ecomaterials, Institute of Environmental Science and Technology, Innovation Centre, Nanyang Technological University, Singapore 637723

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PMMA is one of the most versatile polymeric materials for applications in various technological areas including optics and electro-optics. While the current applications of PMMA in optics and electro-optics are limited by their linear optical behavior, we report here in this paper the unique nonlinear optical behavior of nanohybrids consisting of nanocrystalline TiO₂ in PMMA. Transparent thin films of TiO₂–PMMA nanohybrid on substrates were synthesized by in-situ sol–gel and polymerisation, assisted by spin coating. Using titanium isopropoxide (Ti-iP) as the starting material for nanocrystalline titania, together with methyl methacrylate and 3-(trimethoxysilyl)propyl methacrylate, nanohybrids containing up to 80% Ti-iP in PMMA were successfully realized. The resulting nanohybrid thin films coated on quartz substrates are optically transparent and demonstrate large nonlinear optical behavior, with an ultrafast response of <1.5 ps. The highest two-photon absorption coefficient (β) and nonlinear refractive index (n²) are observed with the nanohybrid thin film of 60 wt% Ti-iP in PMMA, as confirmed by the Z-scan technique.

Introduction

Organic–inorganic hybrid nanocomposites have attracted extensive attention in recent years in the international materials research community. Through the combinations of nano-sized organic and inorganic segments, several new classes of materials with novel physical and chemical properties have been synthesized via different routes. Novel electronic and optical materials based on these nanohybrids have found applications in technologically demanding areas such as optical coatings, contact lenses, optical switches, high refractive index devices, optical waveguides and nonlinear optical devices.

Polymer–titania hybrid nanocomposites for optical applications were previously studied by several researchers. Wilkes et al. successfully prepared triethoxysilane capped polymer–titania hybrid materials, including poly(arylene ether ketone) (PEK) and poly(arylene ether sulphone) (PES). Depending on the titania loading, the refractive indices of PES–TiO₂ and PEK–TiO₂ were in the range of 1.60–1.75. Similar results were also reported later on poly(tetramethylene oxide) (PTMO)–titania hybrids. Zhang et al. synthesized a poly(methyl methacrylate) (PMMA)–titania nanohybrid using a chelating ligand as a coupling agent. However, the titania loading was limited, while large amounts of solvent and chelating agent remained in the resulting material. Hybrid thin film properties were not deeply investigated in their study. A further study on the preparation and optical properties of PMMA–titania thin films was performed by Chen et al., who synthesized thin film PMMA–TiO₂ nanocomposites by an in situ sol–gel process of trialkoxysilane-capped PMMA–titania combined with spin coating and multi-step annealing processes. The refractive indices were in the range of 1.505–1.553. However, the resulting titania loading was limited to 11.7%, because if the

titania loading was above this value the polymerization solution was easily gelled before spin coating into thin films. They suspected that it was due to the fast reaction of titanium alkoxides because of the acid catalyst and insufficient polymerization solvent. Therefore they attempted to increase the titania content in the hybrid thin film by applying a catalyst-free sol–gel process. The amount of titanium alkoxide in the precursor solution was successfully increased up to 90% without any gel formation and the refractive indices of the prepared films were reported to be in the range of 1.505–1.867.

These previous studies were concerned with the measurement of the linear optical refractive index, while the nonlinear optical properties of nanohybrid thin films of TiO₂ in PMMA have not yet been fully explored. Nonlinear optical properties such as fast response time and large third-order nonlinearity (χ(3)) are essential for several current and future optical device applications in optical computing, real time holography, optical correlators and phase conjugators. Therefore the present research work is aimed at studying the effect of titania loading on the nonlinear optical behavior of transparent nanohybrid thin films of TiO₂ in PMMA.

Experimental

Materials

The starting materials in this work were methyl methacrylate (MMA, 99%, Acros), 3-(trimethoxysilyl)propyl methacrylate (MSMA, 98%, Acros), tetrahydrofuran (THF, 99%, Acros), benzoyl peroxide (BPO, 98%, Acros), de-ionized water, ethyl alcohol (EtOH, 95%, Merck), hydrochloric acid (HCl, 36%, Ajax) and titanium isopropoxide (Ti-iP, 98%, Acros).
Preparation of nanohybrid TiO$_2$–PMMA

The synthesis route for the nanohybrid TiO$_2$–PMMA is modified from the technique reported in reference 11, where the monomers, MMA and MSMA, and initiator BPO in THF were added into a reaction flask and polymerized at 60 °C for 1 hour. The molar ratio of MSMA to MMA + MSMA was controlled at 0.25 and the amount of BPO added to the mixture was fixed at 3.75 mol%. At the same time, a TiO$_2$ based sol solution was prepared using titanium isopropoxide (Ti-iP), de-ionized water, ethanol and hydrochloric acid, by following the method described in the literature.\(^{14}\) Titanium isopropoxide (Ti-iP) was first mixed with ethanol in a container and stirred for 30 minutes. A mixture of de-ionized water and HCl was then added under stirring into the transparent solution to promote hydrolysis. The Ti-iP concentration in the solution was controlled at 0.4 M with an understoichiometric ratio of water to Ti-iP of 0.82 and pH value of 1.3 for obtaining a stable solution. Finally, this homogeneous mixture was added dropwise over a duration of 30 minutes into the partially polymerized monomers with rigorous stirring to avoid local inhomogeneities. The reaction was allowed to proceed at 60 °C for another 2 hours. Following this procedure, four transparent solutions, with the weight percentage of titanium isopropoxide of 20, 40, 60 and 80 wt% in PMMA, respectively, were prepared.

In order to form the required thin films, the solutions were each spun coated on quartz substrates at 3000 rpm for 20 seconds. Prior to the spin coating, the substrates were carefully cleaned, first in diluted HNO$_3$ solution in an ultrasound bath. After thorough rinsing in running water, the ultrasound bath treatment was repeated with distilled water, acetone and ethanol. The substrates were then dried and stored in the drying oven at 40 °C. The coated films were then annealed in two stages of curing temperatures to promote the polymerization, i.e. at 60 °C for 30 minutes and 150 °C for 3 hours. For labeling purposes, the resultant transparent polymerization, annealed in two stages of curing temperatures to promote the nanohybrid thin films of TiO$_2$ in PMMA were termed as T$_{20}$, T$_{40}$, T$_{60}$ and T$_{80}$, referring to the amount (wt%) of titanium isopropoxide in the reaction mixture.

Characterization

Linear absorption spectra of these films were measured using UV-Vis spectroscopy (Shimadzu) at the wavelength range 800–200 nm. A surface plasmon resonance (SPR) spectrometer with Kretschmann configuration and a laser beam of 632 nm in wavelength was used to measure the linear refractive index with Kretschmann configuration and a laser beam of 632 nm in 800–200 nm. A surface plasmon resonance (SPR) spectrometer with UV-Vis spectroscopy (Shimadzu) at the wavelength range. Linear absorption spectra of these films were measured using UV-Vis spectroscopy (Shimadzu) at the wavelength range.

Results and discussion

Fig. 1 plots the linear absorption spectra of nanohybrid thin films with four different weight percentages of titanium oxide precursor in PMMA. It shows that all four samples are transparent in the visible region. The onset of absorbance for nanohybrid thin films T$_{20}$, T$_{40}$ and T$_{80}$, as a result of the excitation of electrons from the valence band to the conduction band of TiO$_2$ is observed at the wavelength of about 350–380 nm. However for the case of T$_{60}$, a broader onset is demonstrated in which the absorption edge wavelength of TiO$_2$ is significantly ‘red shifted’. The difference in absorption wavelength indicates a difference in the band gap of TiO$_2$ with increasing loading of the inorganic phase. The band gap energy, $E_g$, of nanohybrids near the absorption edge can be further determined using the following expression:

$$ (x_0^2 h^2) = A (h - E_g) $$

where $x_0$ is the linear absorption of the samples which is normalized to the thickness, $h$ is the incident photon energy and $A$ is a constant.\(^{16}\) The thickness of the samples as determined by SPR spectrometry is 350, 296, 355 and 253 nm for nanohybrids T$_{20}$, T$_{40}$, T$_{60}$ and T$_{80}$, respectively. Fig. 2 shows the intercepts of tangents to the $(x_0^2 h^2)$ versus photon energy ($h$) plots, estimating a band gap energy of 4.72, 4.32, 3.91 and 4.13 eV for T$_{20}$, T$_{40}$, T$_{60}$ and T$_{80}$, respectively. The results here are considerably shifted from the bulk value of 3.20 eV, suggesting that the size of nanocrystallites of titanium oxide in the polymer matrix is very small. Similar behavior was reported for the case of PbS nanoparticles in a polymer composite having a band gap of 2.30 eV, as compared with a bulk value of 0.41.\(^{17}\) Such a shift of the band gap energy can be
confirmed also by observing the shift of the absorption maxima of the spectra in Fig. 1 as the titania content increases. As reported in the literature, the shift of the peak maximum becomes significant when the TiO$_2$ particle size is less than 10 nm. The decrease in band gap energy from 4.72 eV for nanohybrid T20 to 3.91 eV for T60 indicates an increase in the average size of TiO$_2$ nanoparticles, and yet in the range below 10 nm. It is also of interest to note that the band gap energy of nanohybrid thin film T80 is higher than that of T60. This suggests that the crystallite size of TiO$_2$ nanocrystallites in T80 should be smaller than that of T60. This will be further discussed in connection with the results of HRTEM studies and nonlinear optical measurements.

Fig. 3(a) and (b) are bright-field HRTEM micrographs of nanohybrid thin films T60 and T80, showing that they consist of titanium oxide nanocrystallites of ~5–10 nm dispersed in an amorphous phase PMMA matrix. Average crystallite sizes of 6.5 nm and 4.7 nm were measured for T60 and T80, respectively, on the basis of TEM observations. While a rather uniform dispersion of TiO$_2$ particles was achieved in T60 and those with lower TiO$_2$ contents, particle aggregation occurred in T80, where the nanocrystalline TiO$_2$ particles occur as aggregates of ~100–200 nm in size, although their discrete particle sizes are slightly smaller than those of T60. As expected, nanohybrids T20 and T40 exhibited a smaller TiO$_2$ crystal size than that of T60, coupled with a reduced number of TiO$_2$ particles in the PMMA matrix.

The linear refractive indices ($n_o$) of the spin coated nano-hybrid films measured by SPR spectrometer at 632.8 nm were 1.554, 1.618, 1.641 and 1.718 for T20, T40, T60 and T80, respectively. This confirms that increasing the incorporation of titania into the PMMA matrix results in an increment in the refractive index, which is comparable with the results reported by Chen et al. The linear refractive indices ($n_o$) of the spin coated nano-hybrid films measured by SPR spectrometer at 632.8 nm were 1.554, 1.618, 1.641 and 1.718 for T20, T40, T60 and T80, respectively. This confirms that increasing the incorporation of titania into the PMMA matrix results in an increment in the refractive index, which is comparable with the results reported by Chen et al.

Fig. 4 shows the temporal behavior of the photo-induced absorption change of nanohybrids, in which $\Delta T/T$ is the probe transmission as a function of the probe delay. All four nanohybrid thin film samples exhibit a nonlinear optical signal with a very fast characteristic relaxation time of about 1.5 ps. The highest time-resolved $\Delta T/T$ signal is given by nanohybrid thin film T60, followed by T80, T40 and T20, respectively. For comparison, the same experiment was performed on both pure PMMA and TiO$_2$ thin films prepared using the same solution preparation and annealing process. No signals were observed from those samples.

In order to confirm the observed pump-probe result, Z-scan measurements were conducted. An open aperture Z-scan was performed to obtain the two-photon absorption coefficient by assuming the total nonlinear absorption effect as $\alpha = \alpha_0 + \beta I$ and the employed laser beam is Gaussian in space and time. Normalized transmission $T_n(z)$ for open aperture Z-scan is described as follows:

$$T_n(z) = \frac{C(1 + z^2/\xi_0^2)}{\sqrt{\pi}b_0L_{eff}} \int_{-\infty}^{\infty} \ln(1 + q_0e^{-b_0})dt$$

where $\beta$ is the two-photon absorption coefficient, $I_0$ is the on-axis intensity of the laser beam at focus, $C$ is a normalization constant, $L_{eff} = [1 - \exp(-z_0L)]/\alpha_0$ is the effective thickness, $\alpha_0$ is the linear absorption coefficient, $L$ is the sample thickness, and $z_0$ is the diffraction length of the laser beam, defined by $z_0 = \theta_0^2/\lambda$, where $\theta_0$ denotes the beam waist, $\lambda$ the laser wavelength and $q_0 = \frac{b_0L_{eff}}{1 + L_{eff}}$.

In order to exclude the linear transmission of the sample, it is necessary to normalize the transmission $T_n(z)$. The two-photon
absorption coefficient ($\beta$) is determined by fitting eqn. (2) to the experimental open aperture Z-scan data of $T_0(z)$. The measured normalized transmissions are shown in Fig. 5. The curves are nearly symmetrical and have a minimum at $z = 0$ which indicates that $\beta$ is positive. This figure also shows that the $\beta$ value of nanohybrids increases with increasing titanium oxide content up to the maximum which is given by nanohybrid T80. A further increase in titanium oxide content as given by nanohybrid T80, however, provided a decrease. Values of $\beta$ of 160, 510, 1400 and 550 cm GW$^{-1}$ were then obtained for nanohybrid thin films T20, T40, T60 and T80, respectively.

The nonlinear refractive index ($n_2$) was obtained by dividing the data of a closed aperture Z-scan by that of an open aperture Z-scan, both Z-scans being performed at the same incident intensity. By measuring the resultant curve of the difference between the peak and the valley of the normalized transmission ($\Delta T_{p-v}$), the nonlinear refractive index $n_2$ was calculated by the following equation:

$$n_2 = \frac{\Delta T_{p-v}(z/2\pi)}{0.4066/(1-S)^{1/2} L_{eff}}$$  \hspace{1cm} (3)

where $S = 1 - \exp(-2r_0^2/\omega_0^2)$ is the linear aperture transmission with $r_0$ and $\omega_0$ being the aperture and the beam radii, respectively. Fig. 6 shows the experimentally observed closed aperture Z-scans for all four transparent nanohybrid thin films of TiO$_2$ in PMMA. They all show positive nonlinearity, i.e., the normalized transmission exhibits a pre-focal transmission minimum (valley), followed by a post-focal transmission maximum (peak). Similarly to the open aperture experiments, they also exhibit a strong dependence on the weight percentage of titanium oxide in PMMA. Again, the nonlinearity increases with increasing titanium oxide content to reach a maximum value which is provided by thin film T60. The calculated values of the nonlinear refractive indices ($n_2$) for T20, T40, T60 and T80 are $0.17 \times 10^{-2}$, $0.90 \times 10^{-2}$, $2.50 \times 10^{-2}$ and $1.00 \times 10^{-2}$ cm$^2$ GW$^{-1}$, respectively.

The imaginary and real parts of the third-order nonlinear optical susceptibility of a nonlinear optical material can be calculated using the relationship between the two-photon absorption coefficient ($\beta$) and nonlinear refractive index ($n_2$), which is defined as follows:

$$\text{Im}(\chi^3) = \left(n_0^2 \frac{\rho}{2\pi} \frac{\omega_0}{\lambda} \beta \right)$$  \hspace{1cm} (4)

and

$$\text{Re}(\chi^3) = \frac{n_0^2}{0.0395} n_2 (\text{cm}^2 \text{ W}^{-1})$$  \hspace{1cm} (5)

where $n_0$ is the linear refraction index, $\omega_0$ is the vacuum permittivity ($\sim 8.854 \times 10^{-12}$ F m$^{-1}$), and $c$ is the velocity of light in a vacuum ($3 \times 10^8$ m s$^{-1}$). For the calculation, the linear refractive index ($n_0$) of nanohybrid thin films at 780 nm was estimated using a simulation program carried out on the data obtained by SPR spectroscopy at 632 nm. The simulation results provided $n_0$ at 780 nm as 1.537, 1.603, 1.626 and 1.704 for nanohybrid thin films T20, T40, T60 and T80, respectively.

The calculated $\text{Re}(\chi^3)$ for T20, T40, T60 and T80 are $1.0 \times 10^{-10}$, $6.0 \times 10^{-10}$, $17.0 \times 10^{-10}$ and $7.5 \times 10^{-10}$ esu while $\text{Im}(\chi^3)$ are $0.9 \times 10^{-10}$, $3.2 \times 10^{-10}$, $8.9 \times 10^{-10}$ and $3.9 \times 10^{-10}$ esu, respectively. Apparently the imaginary part of the third-order susceptibility is smaller than the real part, which agrees with the two-band theory.

The absolute values of the third-order susceptibility ($\chi^3$) of these thin films were calculated by using the following equation:

$$\chi^3 = \left|\text{Re}(\chi^3)^2 + \text{Im}(\chi^3)^2\right|^{1/2}$$  \hspace{1cm} (6)

and they were $0.14 \times 10^{-9}$, $0.67 \times 10^{-9}$, $1.93 \times 10^{-9}$ and $0.84 \times 10^{-9}$ esu for T20, T40, T60 and T80, respectively. Apparently the $\chi^3$ value for T60 film is about two-fold higher than that of the inorganic composition of TiO$_2$–SiO$_2$ reported by Zhou et al.19

From the pump-probe technique and Z-scan measurement results, it is obvious that the nonlinear optical properties of nanohybrid thin films of TiO$_2$ in PMMA show a strong dependence on the titanium oxide loading. Similar behavior was obtained by Wang et al.20 who observed that the nonlinear absorption of poly(styrene maleic anhydride)/PSMA–TiO$_2$ nanocomposites increased as the weight percentage of TiO$_2$
increased from 15 to 43.9%. The explanation of such nonlinearity behavior can be based on nanometer-sized particles having a higher refractive index in the surrounding environment with lower refractive index. As a result of the large interface of TiO₂ nanoparticles, when wrapped in PMMA which possesses a smaller dielectric coefficient, there will be a strong electric-field charge interaction between them resulting in an electric dipole layer at the nanoparticle surface. This effect can be considered as a dielectric confinement effect or surface polarization, which in turn accelerates the separation of excited charges and enhances the electric field inside the nanoparticles.\textsuperscript{21,22} The lower energy TiO₂ nanoparticles will absorb two photons of energy to transfer to the higher energy state, resulting in an accumulative result of two-photon absorption (TPA). In terms of the atomic bonding, the origin of the nonlinear refractive index may be due to the hyperpolarizability of Ti–O pairs, as reported by Zhu \textit{et al.} for TiO₂-containing glass.\textsuperscript{23} More specifically, the present study shows that there is an optimum concentration of nanocrystalline TiO₂ in the nanohybrids, which may give the strongest response for nonlinear optical behavior. This is provided by composition T60 which is synthesized by incorporating 60 wt% titanium alkoxide in the reaction mixture. Studies using HRTEM confirmed that the nanohybrid consists of titanium oxide nanocrystallites of \( \sim 5-10 \) nm in size. Its UV-Vis spectrum, as compared to those of T20 and T40, also suggests that this is the size range for the nanoparticles in PMMA synthesized in this work. The blue shifts in the spectra of T20 and T40 further indicate a smaller particle size in these two compositions.

In the case of nanohybrid T80, as mentioned before, UV-Vis studies suggested that the nanoparticles of TiO₂ were smaller than those in T60. However this is contrary to the expectation that a higher titanium oxide loading in the precursor would encourage a larger crystallite size. However, its nonlinear optical response, as compared to that of T60, suggests the opposite. This can be accounted for by the consideration that a too high loading of titanium alkoxide can lead to formation of a network consisting of hydrolyzed titanium alkoxides, instead of individual oxide nanoparticles. This has been confirmed by studies using HRTEM. As shown in Fig. 3(b), the nanocrystal-line particles in T80 occur as aggregates of \( \sim 100-200 \) nm in size, while their discrete particle sizes are slightly smaller than those in T60. A similar result was observed using field emission scanning electron microscopy by Chen \textit{et al.}\textsuperscript{11} showing long TiO₂ segments of 100-400 nm in the thin film containing 90 wt% of hydrolyzed titanium butoxide in the PMMA matrix. As a consequence, the quantum confinement effect responsible for nonlinear optical responses decreased remarkably. In addition, the annealing of the spin coated films at 150 °C was not sufficient to transform the network of hydrolyzed titanium alkoxide into discrete crystallites of titanium oxide. This has been confirmed with the FTIR spectra on nanohybrids of TiO₂ in PMMA by Chen \textit{et al.}\textsuperscript{11} demonstrating the occurrence of the Ti–OH absorption band in the range of 3400–3500 cm\(^{-1}\). This explains why a nonlinear optical signal was not observed in TiO₂ thin films, in contrast to the result obtained by Hashimoto \textit{et al.}\textsuperscript{24} on sol-gel films of TiO₂, which provides \( \chi^2 \) values of 4.0 \( \times 10^{-12} \) and 2.4 \( \times 10^{-12} \) esu for rutile and anatase, respectively.

Conclusions

Transparent nanohybrid thin films consisting of nanocrystalline TiO₂ particles in PMMA and of 250 to 350 nm in thickness were successfully synthesized by in-situ sol-gel and polymerization assisted by spin coating, using titanium isoproxipoxide (Ti-iP) and methyl methacrylate and 3-(trimethoxysilyl)propyl methacrylate as the starting materials. They demonstrate unique nonlinear optical behavior, where temporal behavior is shown for the time-resolved probe difference transmittance, with a very fast characteristic relaxation time of \( \sim 1.5 \) ps. Their two-photon absorption coefficient increases with the loading of Ti-iP in PMMA, from 160 cm GW\(^{-1}\) for 20 wt% Ti-iP, up to 1400 cm GW\(^{-1}\) for 60 wt% Ti-iP, whereas there follows a fall in the nonlinear absorption at 80 wt% Ti-iP. The observed nonlinear optical behavior can be accounted for by the nature of nanocrystalline TiO₂, which has exhibits a much higher refractive index than that of the surrounding polymeric matrix. The transparent nanohybrid thin films exhibit an onset of absorbance in the range of 350 to 380 nm, increasing with rising Ti-iP loading up to 60 wt%, and thereafter there follows a decrease at 80 wt%. Accordingly, the band gap decreases from 4.72 eV for 20 wt% Ti-iP in PMMA to 3.91 eV for 60 wt% Ti-iP, again indicating the nanocrystalline nature of the TiO₂ particles, which were observed to be \( \sim 5.0 \) to 10.0 nm in size by HRTEM.

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