The Effects of Additive TiO₂ Nanoparticles on the Energy Gap of DCM Doped with PS Thin Films

Jafer Fahdel Odah

Department of Physics, College of Science, University of Al-Muthanna, Samawa, Iraq

E-mail: hajasafa@yahoo.com

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Abstract. In this work thin films containing laser dye (DCM) doped with polystyrene (PS) were prepared using casting method. Titania (TiO₂) nanoparticles also were synthesized using sol gel technique. Characteristics of the titania were done using XRD pattern, and the characteristic peak of anatase is sharper and clear to observe, in particular at 25.40° degree. While scanning electron microscopy (SEM) was used to achieve the morphology of TiO₂ samples, and to determine the sizes of nanoparticles. Different titania nanoparticle densities (0.882×10^{20} , 1.765×10^{20} , 2.648×10^{20} , 3.530×10^{20} and $4.413 \times 10^{20} \text{ cm}^{-3}$) were co-doping with dye doped polymer and study the effect of this addition on the optical properties and electronic transition energy gaps in cases of both direct and indirect transitions.

Introduction

Composite materials obtained by integrating two or more materials can offer the potential to have performance far beyond those of the basic constituents. There are a variety of particulate substances, such as metallic, ceramic, carbon, etc., that can be used as dopants in materials [1, 2]. In particular, polymeric materials are of interest for doping with a variety of dopants and form composites with unique properties. Particle dopants can be of different shapes, such as spherical [3], fiber-like [4], or flake-platelets and with dimensions from nano- [5] to micron-sized particles [6]. These heterogeneous mixtures exhibit improvements in their properties compared to those of the neat polymer host in terms of mechanical, electrical, and thermal properties, tailoring them to a variety of applications [7,8].

Most organic polymers show a limited refractive index, in the range 1.35-1.5. For optical applications, polymers with higher refractive index are required [9]. In the last years, the polymer doped with metal oxide nanoparticles have been studied as alternative materials for optical applications, including planar waveguide devices and microoptical elements [10-11]. The polymers modified by metal oxide nanoparticles have been prepared by sol-gel process, by polymerization of monomer containing nanoparticles and by dispersing of nanoparticles in a polymeric matrix [12-13]. The presence of nanoparticles in polymer improves the mechanical, electrical and optical properties of the material and it is possible to control these properties, including the refractive index, by concentration [14].

In the literature, several reports have appeared on TiO₂ thin films produced by different techniques. Sayilkan et al. [15] reported the preparation of TiO₂ thin films by thermal hydrolysis. Sankapal et al. [16] described the synthesis of nanocrystalline titanium dioxide thin films and powders by chemical and electrochemical deposition methods. Venkatachalam et al. [17] prepared nanocrystalline TiO₂ photocatalysts of different anatase to rutile ratios by a sol-gel technique. There are large variations in the properties of TiO₂ thin films produced by each technique. However, the production of anatase TiO₂ phase is not trivial, and represents an interesting case where synthesis of TiO₂ on the nanometric scale favors the anatase phase over rutile [18]. Thus, synthesis methods able to control the final particle size are necessary for development of the phase [19].

The preparation of polymer films containing dispersed metallic clusters or metallic nanoparticles has been of great interest, and a review article on this topic was published as early as 1995 [20].

Titanium dioxide (TiO₂) nanoparticles have grasped a great attention their worldwide due to their potential applications [21]. They have demonstrated unique properties such as high absorption ability and good photocatalytic activity [22]. In this work TiO₂ nanoparticles were prepared using sol-gel method, and then co-doped with the mixture of DCM laser dye and PS polymer solutions to obtain the final samples.

Organic polymers were also used as hosts to the organic dyes because these transparent polymers have optical homogeneity [23]. The optical properties of DCM doped with PS polymer by A. N. Mohamed [24], he find out that the direct energy gap was 3.9eV for PS thin film, energy gap for PS-DCM thin film was 2.2eV. While for indirect transitions the energy gap for PS thin film was 2.25eV and phonon energy was 0.55eV, but the energy gap for PS-DCM film was 1.4eV and phonon energy was 0.5eV.

The increase of the polymer solution solidity prevents the degradation process of the excited dye molecules that results from photochemical reactions. Consequently, the stability of the dye increases and the fluorescence intensity increases as well. This is due to the dimers decomposition which terminates the absorption process that occurs in the same region of fluorescence resulting from re – absorption [25].

The most important reasons to use the solid matrix as a host material for dyes is due to its obvious advantages such as rigidity and compactness, lack of toxicity and solvent evaporation [26]. Some important characteristics gave polymers forefront to be a host for dyes which possess many favorable optical properties in comparison with other type of solid hosts. The high homogeneity of polymers is important for narrow line width oscillators, and one can quite effectively control the chemical composition at the formation stage, and they show much better compatibility with organic laser dyes [27].

One of the important organic materials that used in this study is the fluorescent dyes, which are organic molecules with aromatic ring structures, which possess delocalized π electrons that can be easily excited by photons [28]. The organic laser dye used in this work is DCM, [2-[2-[4-(dimethylamino)phenyl]ethenyl]-6-methyl-4H-pyran-4-ylidene]-propanedinitrile and the chemical formula is C₁₉H₁₇N₃O, wich mixed with TiO₂ nanoparticles synthesized via sol-gel method and doped with PS polymer of the chemical formula (C₈H₈)_n to prepare thin films.

Experimental part

Laser dye solutions were prepared by dissolving the required amount of the DCM dye in alcohol in order to obtain the final concentration of dye solution was 5×10^{-3} mol/liter.

Titanium dioxide nanoparticles were prepared by using the sol-gel method with 10 ml titanium alkoxide), as the raw material, mixed with 40 ml 2-propanol in a dry atmosphere. This mixture was then added dropwise into another mixture consisting of 10 ml water and 10 ml 2-propanol, in order to investigate the effect of pH upon the sample properties, hydrochloric acid or ammonium hydroxide was added, which adjusted the acidity-alkalinity of the gel the value of pH3. A yellowish transparent gel was formed after one hour stirring, the obtained gel then dried at 105°C for several hours until it turned into a yellow block crystal. Calcinations of the synthesized materials were carried out at 500°C for six hours in a furnace.

The nanopowder structure were analyzed with a Shimadzu 6000 X-ray diffractometer using Cu K α radiation ($\lambda=1.5406\text{\AA}$) in reflection geometry. A proportional counter with an operating voltage of 40 kV and a current of 30 mA was used. XRD patterns were recorded at a scanning rate of 0.08333° s⁻¹ in the 2 θ range (20° - 60°). While scanning electron microscopy (SEM) was used to achieve the morphology of TiO₂ samples, and to determine the sizes of nanoparticles. SEM measurements of type (Σ IMA, Germany), which a focused beam of electrons to generate an image or to analyses the surface of specimen.

To prepare PS doped with DCM thin films, firstly dissolving 0.015gm from DCM in 10ml THF solvent and stirrer about 30 minutes to obtain homogenous solution, then 2gm PS dissolve in 30ml THF with 2 hours vigorous stirring to get the polymer solution. To synthesis the final thin

films, 1ml DCM solution mixed with 5ml PS solution and casting on glass substrate at room temperature. Then different particle densities of obtained TiO_2 nanoparticles: (0.882×10^{20} , 1.765×10^{20} , 2.648×10^{20} , 3.530×10^{20} and $4.413 \times 10^{20} \text{ cm}^{-3}$) were suspended in THF solvent and added to the mixture of DCM-PS. The final films labeled as (A, B, C, D, and E) respectively as the nanoparticles density increasing respectively.

Thin films thickness was measured using the optical interferometer method employing He-Ne laser $0.632 \mu\text{m}$, and found to $0.45 \mu\text{m}$ for all samples.

The optical absorption and transmission spectra of DCM doped with PS thin films were recorded using UV-VIS double beam spectrometer in the wave length range from 190 to 1100 nm. The absorption coefficient (α) was calculated using the equation [29]

$$\alpha = \frac{2.303}{d} A, \quad (1)$$

where: α : Absorption coefficient, A: Absorbance, d: thickness of the thin film.

The direct allowed and forbidden transitions happen between near top points of valance band (V.B.) and bottom points of covalent band (C.B.), the absorption coefficient for this transitions type given by [30]

$$\alpha h\nu = B(h\nu - E_g)^r, \quad (2)$$

where: E_g : energy gap between direct transition, B: constant depended on type of material, ν : frequency of incident photon, r: exponential constant, its value depended on type of transition, $r = 1/2$ for the allowed direct transition, $r = 3/2$ for the forbidden direct transition.

While in case of indirect allowed and forbidden transitions, the bottom of (C.B.) is not over the top of (V.B.), the electron transits from (V.B.) to (C.B.) not perpendicularly where the value of the wave vector of electron is not equally before and after transition of electron. This transition type happens with helpful of a like particle is called "Phonon", for conservation of the energy and momentum law. The absorption coefficient for transition with phonon absorption is given by [31]

$$\alpha h\nu = B(h\nu - E_g \pm E_{ph})^r \quad (3)$$

where E_g : energy gap for indirect transitions, E_{ph} : energy of phonon, is (+) when phonon absorption and (-) when phonon emission, ($r = 2$) for the allowed indirect transition, ($r = 3$) for the forbidden indirect transition.

The reflective index (n) of the thin films calculated from the equation [32]

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (4)$$

where: n: Reflective index, R: Reflectance.

The extinction coefficient can be calculated in terms of the absorption coefficient using the equation [33]

$$K = \frac{\alpha \lambda}{4\pi} \quad (5)$$

The real and imaginary complex dielectric constant can be expressed by equations (6, 7) respectively [34, 35]

$$\epsilon_r = n^2 - K^2 \quad (6)$$

$$\epsilon_i = 2nK \quad (7)$$

The optical conductivity of thin films can be calculated using the equation [36]

$$\sigma = \frac{\alpha n c}{4\pi} \quad (8)$$

Results and Discussions

XRD spectrum of the TiO_2 nanoparticles which synthesized via sol-gel technique at pH3 and calcination of the synthesized material was carried out at temperature of 500°C for 6 hours in furnace shown in figure 1.

The anatase phase was identified at 2θ of 25.40° , 38.10° , 48.20° , 53.90° and 55.10° degrees, and the characteristic peak of anatase is sharper and clear to observe, in particular at 25.40° degree.

Figure 1. XRD spectrum of TiO_2 nanoparticles

The scanning electron microscope (SEM) image of TiO_2 nanoparticles is presented in figure 2. Titania particle size determination was carried out with (SEM) after preparing TiO_2 at pH3 and 500°C calcination temperature, the nanoparticles then suspend as film using spin coating process. The corresponding value of the TiO_2 nanoparticles size is about (55nm).

Figure 2. Scanning electron microscope of the TiO_2 nanoparticles

The absorption spectra for PS doping with DCM and TiO_2 nanoparticles thin films at room temperature shown in figure 3. It is clearly shown that appear single peak at 506nm and it is obviously that the absorbance increases with increasing titania nanoparticles density increasing, this is refer to increase the number of titania nanoparticles that is denominate and decrease the role of polymer or due to aggregates such as dimmers.

Figure 3. Absorbance for PS doped with DCM thin films mixed with different particle density of titania nanoparticles

Reflectance spectra for prepared thin films were recorded at room temperature and illustrated in figure 4. One can observe from the reflectance spectra that the increasing in the nanoparticles density leads to decreasing in intensity of reflection, it is suggested that the presence of titania nanoparticles in starch-based polymer improved the UV-shielding property of the polymer.

Figure 4. Reflectance for PS doped with DCM thin films mixed with different particle density of titania nanoparticles

Figure 5 shows the absorption coefficient for PS doped with DCM thin films mixed with different particle density of titania nanoparticles, which determined from absorbance measurements using equation (1)

Figure 5. Absorption coefficient for PS doped with DCM thin films mixed with different particle density of titania nanoparticles

The absorption coefficient of PS doped with DCM thin films mixed with different particle density of titania nanoparticles increases sharply in the UV and visible region range, and then decreased gradually in the end of visible region because it is inversely proportional to the transmittance. This can be linked with increase in grain size and it may be attributed to the light scattering effect for its high surface roughness [37].

The energy gap can be calculated from equations (2) and (3), the relations are drawn between $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$ and photon energy ($h\nu$), as in figure 6 illustrates allowed direct transition electronic and figure 7 illustrates allowed indirect transition electronic. The energy gap value depends on the films deposition conditions.

Figure 6. Relationship between $(\alpha h\nu)^2$ and photon energy (e.V)

Figure 7. Relationship between $(\alpha h\nu)^{1/2}$ and photon energy (e.V)

The energy gap values for direct and indirect for all thin films are summarized in table 1.

Table 1. Electronic transitions energy gap (e.V) and phonon energy (e.V) for PS doped with DCM thin films.

Sample	Particle density of $\text{TiO}_2(\text{cm}^{-3})$	Allowed direct band gap (e.V)	Allowed indirect band gap (e.V)	Allowed indirect phonon energy (e.V)
A	0.882×10^{20}	2.28	0.125	1.875
B	1.765×10^{20}	2.255	0.18	1.7
C	2.648×10^{20}	2.22	0.22	1.62
D	3.530×10^{20}	2.2	0.3	1.42
E	4.413×10^{20}	2.14	0.38	1.26

From table 1 and the figures 6 and 7, it can be observed that (E_g) in direct transitions is decreasing with the increasing of titania nanoparticles density for all films. Particle density led to increased levels of localized near valence band and conduction band and these levels ready to receive electrons and generate tails in the optical energy gap and tails is working toward reducing the energy gap.

The refractive indices of PS doped with DCM thin films mixed with different particle density of titania nanoparticles are determined from equation (4). Figure 8 shows the variation in refractive index of PS doped with DCM thin films mixed with different particle density of titania nanoparticles in the wavelength range of (300-800) nm. The increase in the titania particle density results in a decrease in the refractive index in the visible region. And the refractive index increases as the wavelength increases in the infrared range. This trend shows an increase of the value of refractive index with higher particle density. The increase may be attributed to higher packing density of the films and hence caused change in the refractive index.

Figure 8. Refractive Index against the Wavelength(nm)

The extinction coefficient (K) is directly related to the absorption of light then related to absorption coefficient by the equation (5), so (K) can be measured by using the previous relation. The curves of extinction coefficient for PS doped with DCM thin films are shown in figure 9. Extinction coefficient behaves in the same behavior of absorption coefficient because they are joined by previous relation, extinction coefficient increasing with increasing of particle density.

Figure 9. Extinction coefficient against the Wavelength(nm)

Both real (ϵ_r) and imaginary (ϵ_i) dielectric constant are measured for prepared films by using relations (6) and (7) respectively. Figures 10 and 11 illustrate variation of (ϵ_r) and (ϵ_i) as a function of wavelength. The figures show that in all samples the real part behaves like the refractive index because of the smaller value of (K^2) compared to (n^2), while (ϵ_i) depends mainly on the (K).

Figure 10. Real part dielectric constant against the wavelength(nm)

Figure 11. Imaginary part dielectric constant against the wavelength(nm)

Figure 12. Optical conductivity as a function of photon energy

Figure 12 shows the variation of optical conductivity as a function of photon energy for different titania nanoparticle density. The optical conductivity is calculated by using equation (8). From figure 12, one can see that the optical conductivity increases with increasing photon energy. This suggests that the increase in optical conductivity is due to electron excited by photon energy, and the optical conductivity of the films increases with increasing of particle density. High absorption of thin film behavior is due to the photon-atom interaction. This effect increases the optical conductivity.

Conclusions

Nanostructured titanium dioxide is prepared using sol gel method and doping in the DCM/PS matrix, was directly affected on the optical properties of the PS thin films. The optical absorption coefficient (α) of PS doped with DCM thin films mixed with different particle density of titania nanoparticles is about ($\alpha > 10^3 \text{ cm}^{-1}$), thus absorption coefficient has higher increase at wavelength ($\lambda < 400 \text{ nm}$). This converts to a large probability that direct electronic transition will happen. Also these films have allowed direct transition and allowed indirect transition. Increasing of the particle density for all films cause a decrease in the optical band gap value and an increase in the optical constants refractive index, extinction coefficient, real and imaginary parts of the dielectric constant and optical conductivity.

Reference

- [1] A. Maaroufi, K. Haboubi, A. El Amarti, F. Car-mona, Electrical resistivity of polymeric matrix loaded with nickel and cobalt powders, *Journal of Materials Science* 39(2004),265–270.
- [2] Y. Xi, H. Ishikawa, Y. Z. Bin, M. Matsuo, Positive temperature coefficient effect of LMWPE-UHMWPE blends filled with short carbon fibers, *Carbon* 42 (2004), 1699–1706.
- [3] H. Zois, Y. P. Mamunya, L. Apekis, Structure and dielectric properties of a thermoplastic blend containing dispersed metal, *Macromolecular Symposia* 198(2003),461–472.
- [4] M. Moniruzzaman, K. I. Winey, Polymer nanocomposites containing carbon nanotubes, *Macromolecules* 39(2006), 5194–5205.
- [5] T. W. Ebbesen, Carbon Nanotubes, *Annual Review of Materials Science* 24(1994), 235–264.
- [6] H. Zois, L. Apekis, Y. P. Mamunya, Structure-electrical properties relationships of polymer composites filled with Fe-powder, *Macromolecular Symposia* 194 (2003), 351–359.
- [7] R. Schueler, J. Petermann, K. Schulte, H. P. Wentzel, Agglomeration and electrical percolation behavior of carbon black dispersed in epoxy resin, *J. App. Poly. Sci.* 63(1997), 1741–1746.
- [8] J. L. Alan kin-tak Lau, *Multifunctional Polymer Nanocomposites*, Taylor and Francis Group, LLC, (2011).
- [9] Wang Y., Flaim T., Mercado R., Fowler S., Holmes D., Planje C." Hybrid high refractive index polymer coatings": *Proceedings of SPIE* 5724 (2005), 42-49.
- [10] Cheong W. C., Yuan X. C., Koundriachov V., Yu W. X.: *Opt. Express*, 10(2002), 586.
- [11] Kim W. S., Yoon K. B., Bae B. S.: *J. Mater. Chem.*, " Nanopatterning of photonic crystals with a photocurable silica–titania organic–inorganic hybrid material by a UV-based nanoimprint technique" 15(2005), 4535-4539.
- [12] García-Moreno I., Costela A., Cuesta A., García O., del Agua D., Sastre R.: J. " Synthesis, Structure, and Physical Properties of Hybrid Nanocomposites for Solid-State Dye Lasers" *Phys. Chem. B*, 109 (2005), 21618-21626.
- [13] Lin D. J., Chen C. C., Su Y. C., Huang S. H., Cheng L. P. " Preparation of silica-filled poly(2-hydroxymethyl methacrylate) nanocomposites cured by photoirradiation during the sol–gel process": *J. Appl. Polym. Sci.*, 94 (2004), 1927-1935.
- [14] Vollath D., Szabo D. V." Synthesis and Properties of Nanocomposites": *Adv. Eng. Mater.*, 6 (2004), 117-127.

-
- [15] F. Sayilkan, M. Asilturk, P. Tatar, N. Kiraz, S. Sener, E. Arpac, H. Sayilkan, " Photocatalytic performance of Sn-doped TiO₂ nanostructured thin films for photocatalytic degradation of malachite green dye under UV and VIS-lights" Mater. Res. Bull. 43(2008), 127–134.
- [16] B.R. Sankapal, S.D. Sartale, M.C. Lux-Steiner, A. Ennaoui, C. R. " Chemical and electrochemical synthesis of nanosized TiO₂ anatase for large-area photon conversion" Chimie 9 (2006) 702-707.
- [17] N. Venkatachalam, M. Palanichamy, V. Murugesan, "Sol–gel preparation and characterization of nanosize TiO₂: Its photocatalytic performance" Mater. Chem. Phys. 104(2007) 454-459.
- [18] C. Ribeiro, C. Vila, J.M.E. Matos, J. Bettini, E. Longo, E.R. Leite, " Role of the Oriented Attachment Mechanism in the Phase Transformation of Oxide Nanocrystals" Chem. Eur. J. 13 (2007) 5798-5803.
- [19] C. Ribeiro, C. Vila, D.B. Stroppa, J. Bettini, V.R. Mastelaro, E. Longo, E.R. Leite, "Anisotropic Growth of Oxide Nanocrystals: Insights into the Rutile TiO₂ Phase" J. Phys. Chem. C 111(2007) 5871-5875.
- [20] D.Y. Godovski, " Electron behavior and magnetic properties of polymer nanocomposites" Adv. Polym. Sci. 119 (1995) 79–122.
- [21] L. Saadoun, J. A. Ayllon, J. Jimenez- Becerril, J. Peral, X. Domenech, and R. Rodriguez-Clemente, Mater. Res. Bull. 35(2000) 193.
- [22] Yu-Chang Liu, Yun-Fang Lu, Yz-Zhen Zeng, Chi-Hung Liao, Jen-Chieh Chung, and Tsong-Yang Wei, "Nanostructured mesoporous titanium dioxide thin film prepared by sol-gel method for dye sensitized solar cell", International journal of photo energy, 2011(2011)9.
- [23] S. Popov, " Dye photodestruction in a solid-state dye laser with a polymeric gain medium "Appl. Opt. 37,(1998) 6449-6455.
- [24] Ahmed Namah Mohamed Studying the optical properties of thin films prepared from polystyrene doped with DCM dye, 61 (2015)176-181
- [25] F. Amat-Guerri, A. Costela, J. M. Figuera, F. Florido, and R. Sastre, "Laser action from rhodamine 6G-doped poly (2-hydroxyethyl methacrylate) matrices with different cross linking degrees", Chem. Phys. Lett., 209,(1993) 352
- [26] R.J. Nedumpara, B. Paul, A. Santhi, P. Radhakrishnan and V.P.N. Nampoori, "Photoacoustic Investigations on the Photostability of Coumarin 540-Doped Pmma", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 60(2004) 1–2.
- [27] A. Costela, I. Garcia-Moreno, C. Gomez, M. Alvarez, F. Amat-Guerri, M. Liras, and R. Sastre, "New Efficient and Stable Polymeric Solid State Lasers Based on Modified Dipyrromethene.", BF₂ complexes SPIE, 5460(2004).
- [28] R.P. Haugland, "Handbook of Fluorescent Probes and Research Chemicals", Molecular Probes: Eugene, OR. (1999).
- [29] G. Streetman Banerjee, "Solid State Electronic Devices" the university of Texas at Austin,(2006)
- [30] C. Kittel, "Introduction to Solid State Physics," 5th ed., Willy, New York, (1981).
- [31] D. Neamen, "Semiconductor Physics and Devices," University of New Mexico, (1992).
- [32] J. I. Pankove, Prentice Hall, New York, (1971)
- [33] Ulrich, H., "Introduction to Industrial Polymers" New York, (1982)
- [34] M. Balkanski, "Optical Properties of Solids" vol2, Amsterdam, New York. Oxford (1992)
- [35] B. O Seraphin, "optical Properties of solid New Developments" company, American, Elsevier Publishing-New York, (1976).
- [36] Y.T. Ravikiran, M.T. Lagare, M. Sairam, N.N. Mallikajuna, B. Sreebhar , S. Manohar , A.G. MacDiarmid, and T.M. Aminabhavi, " Synthesis, characterization and low frequency AC conductivity of polyaniline/niobium pentoxide composites", Synthetic Metals 156, (2006)1139-1147.
- [37] S. Karvinen, "The Effect of Trace Element Doping of TiO₂ on the Crystal Growth and on the Anatase to rutile Phase Transformation of TiO₂," Solid State Sciences, 5, (2003) 811-819.