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College of Education
Department of Physics*



*Study the Characteristics and Nonlinear
Optical Properties of Semiconductors
Prepared by Pulsing Laser Ablation*

A Thesis

*Submitted to the Deanery of College of Education at
Al- Qadisiyah University in Partial Fulfillment of the
requirements for the Degree of M. Sc. Science in Physics*

by

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ قَالُوا سُبْحَانَكَ لَا عِلْمَ لَنَا إِلَّا مَا عَلَّمْتَنَا

إِنَّكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ ﴾

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[سورة البقرة: الآية 32]

Dedication

To the great teacher of humanity prophet Muhammad (pbuh).

To my lady Fatima Al-Zahraa (peace be on her).

To the martyrs of Popular Mobilization.

To My family who stood by me and helped me reaching this stage.

To my brothers for his help.

Murtadha

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Abstract

This thesis presents an easy, fast and one-step effective method to preparation and characterization of the linear and nonlinear optical properties of pure and stable semiconductor nanoparticles in a high ablation rate and size-selected manner with a high concentration, nontoxic and contamination.

First: the nanoparticles suspended in a colloid solutions synthesized by pulsed (Q-switched) Nd-YAG laser ablation of solid piece of cadmium telluride as a target with high purity immersed in distilled water and pure methanol. The preparation parameters used in this work which proved good efficiency in the formation of nanoparticles by PLAL process, which are: number of laser shots is 100, 200 and 300 pulse. Laser energy and wavelength is constant at 100mJ and 1064nm, respectively. Reparation rate and pulse duration is 6Hz and 10ns, respectively. Moreover, the quantity of liquid in the vessel was 2ml.

Second: Polyvinyl Alcohol (PVA) films doping with colloid solutions containing different concentrations of CdTe nanoparticles according to their numbers with different laser shots were fabricated by dropping cast on glass substrate with thickness constant 10 μ m.

X-ray diffraction measurements for all samples showed that the CdTe nanoparticles assembled on the glass substrate had a multi-crystalline structure with a cubic phase at the highest peak in the angle 23.79 $^{\circ}$ according to level (111), with a lattice constant ($a= 6.59$ nm), with relatively increase of grain size of particles. Moreover, XRD measurements of PVA films doped with nanoparticles showed reduction in intensities and disappeared some of peaks, in addition to decrease in the grain size of nanoparticles and an increase of the dislocation density and strain.

The results of the scanning electron microscopy (SEM) of the cadmium telluride nanoparticles that deposited on the glass showed that the prepared samples were composed of irregular spherical structures formed on the surface of the films, while there a slight change in the shapes and sizes of the nanoparticles after doped in polymer where become more spherical accuracy. The results of the

EDX tests showed that colloid solutions prepared was a high purity and containing Cd and Te elements with high ratio as well as their stay after mixing with the polymer in the fabrication of PVA films.

The results of AFM measurement taken into surface topography of nanoparticles showed relatively little variation in the diameters rate of nanoparticles and surface roughness, which was found to increase with the increase in the number of laser pulses. The lowest diameter of the nanoparticles in the methanol solution was obtained. While the diameters of nanoparticles and surface roughness are reduced after doped with polymer.

The influence of the liquid environment and the number of pulses on the optical properties of colloidal nanoparticles and polymer films doped with nanoparticles was studied by Uv-Vis spectrophotometer. The results showed that the absorbance spectrum for colloidal solutions and PVA/NPs films is increased by increasing the number of pulses and changing the values of optical parameters (transmittance, reflectance, optical energy gap, absorption index, refractive index, extinction coefficient, real and imaginary part of the dielectric constant, optical conductivity).

The influence of the media and concentration of CdTe nanoparticles and PVA/CdTe NPs films on the nonlinear optical and optical limiting behavior was studied by z-scan technique using CW laser with 650nm wavelength and output power 50mW. The results showed that all the prepared samples included a nonlinear refractive index with a negative sign, meaning the occur of self-defocusing phenomenon and also occur of the absorption of two-photon phenomenon. The nonlinear refractive index was found to increase with increasing concentration, while the nonlinear absorption coefficient was observed to decrease with increased concentration for all cases. A comparison was made between all samples prepared in the case of colloidal solutions and PVA films doped with nanoparticles in terms of threshold and the amplitude of the optical limiting . It was found had better optical properties and better efficiency with increasing the concentrations of nanoparticles in both colloid solutions and films.

List of Abbreviation

Symbol	Abbreviation
NLO	Nonlinear Optics
LO	Linear Optical
NPs	Nanoparticles
PLAL	Pulsed Laser Ablation in Liquid
Nd-YAG	Neodymium doped Yttrium Aluminum Garnet
LOMO	Highest Occupied Molecular Orbital
HOMO	Lowest Unoccupied Molecular Orbital
CdTe	Cadmium Telluride
PVA	Polyvinyl Alcohol
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
LEDs	Light Emitting Diodes
EEDs	Electronic Emitting Diodes
NLR	Nonlinear Refractive
NLA	Nonlinear Absorption
TPA	Two Photon Absorption
OPL	Optical Limiting
THG	Third Harmonic Generation
FOM	Figure Of Merit
OD	Optical Density
CW	Continuous Wave
VBS	Variable Beam Splitter
OPI	Optical Interference
UV	Ultra Violet Radiation
XRD	X-Ray Diffraction

SEM	Scanning Electron Microscopy
AFM	Atomic Force Microscope
EDX	Energy Dispersive X-ray
DIW	Distilled Water
FWHM	Full Width at Half Maximum
G.S	Grain Size
JCPDS	Joint Committee on Powder Diffraction Standards
RA	Roughness Average
RMS	Root Mean Square (roughness)

List of Physical Symbols and Units

Symbol	Meaning	Unit
T	Transmittance	-
A	Absorbance	-
R	Reflectivity	-
E_g	Energy band gap	eV
α	Absorption coefficient	cm^{-1}
N	Complex refractive index	-
n_o	The linear refractive index	-
K_o	Extinction coefficient	
ϵ	Complex dielectric constant	$\text{J}^{-1}\text{C}^2\text{m}^{-1}$
ϵ_r	Real dielectric constant	-
ϵ_i	Imaginary dielectric constant	-
σ	Photoconductivity	s^{-1}
I_o	Incident light intensity	$\text{eV}/\text{m}^2.\text{s}$
I_T	Transmitted light intensity	$\text{eV}/\text{m}^2.\text{s}$

I_A	Absorbed light intensity	$eV/m^2.s$
I_R	Reflected light intensity	$eV/m^2.s$
c	Light speed	m/s
λ	Wavelength	nm
t	Thickness	cm, nm
$h\nu$	Photon energy	eV
d_{hkl}	The distance between crystal levels	nm
a	Lattice constant	nm
θ	Bragg angle	Degree
hkl	Millar's coefficients	-
β	Full Width at Half Maximum	Rad
δ	Dislocation Density	Line. m^{-2}
S	The strain	
z_0	Rayleigh length	-
E	Electric field	V/m
P	Polarization	Col./ m^2
χ	The linear susceptibility of the material	-
χ^2	second nonlinear optical susceptibility	-
χ^3	The third nonlinear optical susceptibility	-
n_2	Nonlinear refractive index	cm^2/mW
α_2	Nonlinear absorption coefficient	cm/mW
ω_0	The laser beam waist	mm
I	The intensity of the laser	mW/cm^2
p	Power of laser	mW
L_{eff}	The effective length of sample	cm
k	Wave number	m^{-1}
$\Delta\phi_0$	The variation of phase shift	rad
ΔT_{p-v}	The Difference between the normalized peak and valley transmittance	mW

List of Tables

Table	Title	Page
1-1	Classification of solid materials according to the energy gap (E_g) at room temperature	4
1-2	Part of the periodic table	6
1-3	Some physical properties of the CdTe compound	8
3-1	The principle qualities of polymer	56
4-1	Summary of XRD characterization for CdTe nanoparticles ablation in DIW and methanol with different laser shots.	72
4-2	Summary of XRD characterization for PVA films doped with CdTe NPs ablated in DIW and methanol with different laser shots	74
4-3	Summary of AFM characterization for CdTe nanoparticles	79
4-4	Summary of AFM characterization for PVA/CdTe NPs films	83
4-5	Summary of EDX displays of elemental compositions (% wt) of the nanoparticles	87
4-6	Summary of EDX displays of elemental compositions (% wt) of PVA films doped with CdTe NPs	89
4-7	The results of nonlinear optical properties for CdTe NPs suspended in colloidal solutions by Z-scan technique	115
4-8	The results of nonlinear optical properties for PVA/CdTe NPs films by Z-scan technique	120
4-9	The FOM and OD values of the CdTe NPs suspending in a colloid solutions produced in different liquid and at different laser shots	127
4-10	The FOM and OD values of PVA/CdTe NPs which doped with different colloid solutions at different laser shots	127

List of Figures

Figure	Title	Page
1-1	Evolution of band gap diagram of bulk material from molecular structures to exhibit a link to nanomaterials	5
1-2	Crystal structure of cadmium telluride	7
1-3	Schematic draw of the interactions happening in PLAL process; (I) laser-liquid interactions, (II) laser-target interactions, (III) target-liquid interactions, (IV) products-target interaction, (V) laser-products interaction, (VI) liquid-products interaction.	10
2-1	The structure of polyvinyl alcohol (PVA)	19
2-2	Nanometric scale	20
2-3	Classifications of nanomaterials: (a) Zero-dimensional spheres and clusters, (b) One-dimensional nanofibers, wires, and rods, (c) Two-dimensional films, plates, and networks, (d) Three-dimensional nanomaterials	23
2-4	Top down and Bottom up approach for synthesis of nanomaterial	24
2-5	Material removal via vaporization (left), pressure induced melt displacement (middle) and explosive melt ejection (right)	28
2-6	Shadowgraph images of laser ablation phenomena observed for the 18 mM PVP solution. Some remarkable phenomena were selected: (a) optical emissions, (b) shockwave, (c) cavitations bubble and (d) secondary shockwave generated at the bubble collapse	30
2-7	The diffraction pattern of the Bragg	34
2-8	The main regions of the optical absorption edge, (A) The high absorption region, (B) The Exponential absorption region, (C) The low absorption region	36
2-9	The direct and indirect energy gap	39
2-10	The P-E relation for (a) a linear dielectric medium, and (b) a nonlinear medium	44
2-11	Two photon absorption	46
2-12	Nonlinear refraction phenomena: (a) self-focusing and (b) self-defocusing	46

2-13	Third harmonic generation: (a) Geometry of Third harmonic generation. (b) Energy level diagram describing third harmonic generation	47
2-14	Schematic of the basic device of the z-scan technique	48
2-15	The propagation of focused intense radiation through a nonlinear self –focusing medium for a sample placed (a): in front of the focus and (b): behind it	50
2-16	Normalized transmittance in the closed aperture graph for the media with the positive (solid curve) and negative (dashed curve) nonlinear refractive indices	50
2-17	Curves form of Z-scan technique with open aperture, (a).Two photon absorption, (b). Saturated absorption	51
2-18	idea of ideal optical limiting	53
2-19	Transmittance Output of an Ideal Optical Limiter as a Function of the Input power	54
3-1	Comprehensive scheme of experimental work	55
3-2	Ultrasonic cleaning device	58
3-3	Experimental set-up to preparation of NPs by PLAL	58
3-4	Image of Nd-YaG laser device	59
3-5	Schematic diagram drop casting method experimental set up	61
3-6	The Set-up of Z-scan technique (A) Close-aperture system and (B) Open-aperture system	62
3-7	The Set-up of optical limiting system	63
3-8	UV-Visible spectrophotometer (SP-3000 Plus, OPTIMA)	64
3-9	Schematic of thin film thickness measurement	65
3-10	(a) and (b) Images of XRD device, (c) Schematic diagram of the investigation by XRD device	66
3-11	(a) Schematic diagram of a scanning electron microscope, (b) Image of a scanning electron microscope	67
3-12	(a) principle of atomic force microscope, (b) image of AFM device	68
4-1	XRD pattern taken onto the (A) CdTe in its solid state (bulk), CdTe NPs films assembled onto a clean glass substrate (B) produced in DIW and (C) produced in methanol, at same parameters (E=100 mj, λ =1064 nm, F=6Hz and PN (100,300) pules.	70

4-2	XRD pattern taken onto the (A) PVA film in its pure state, PVA films doped with CdTe NPs ablated (B) in DIW and (C) in methanol with different laser shots	73
4-3	AFM images (A) 2D, (B) 3D and (C) size distributions for samples (S1, S2, S3) of CdTe NPs produced in DIW at (100, 200, 300) laser shots and assembled onto a clean glass substrate.	77
4-4	AFM images (A) 2D, (B) 3D and (C) size distributions for samples (S4, S5, S6) of CdTe NPs produced in methanol at (100, 200, 300) laser shots and assembled onto a clean glass substrate.	79
4-5	AFM images (A) 2D, (B) 3D and (C) size distributions of samples (G1, G2, G3) of PVA films doped with CdTe NPs produced in DIW at laser shots of (100, 200, 300) pulse	82
4-6	AFM images (A) 2D, (B) 3D and (C) size distributions of samples (G4, G5, G6) of PVA films doped with CdTe NPs produced in methanol at laser shots of (100, 200, 300) pulse	83
4-7	SEM images of the CdTe nanoparticles synthesized by laser ablation (A) in DIW and (B) in methanol at same parameters (E=100 mj, λ =1064 nm, F=6Hz and 300 pules)	85
4-8	EDX spectra taken onto the CdTe nanoparticles synthesized by laser ablation (A) in DIW and (B) in methanol at same parameters (E=100 mj, λ =1064 nm, F=6Hz and 300 pules)	86
4-9	SEM images of the PVA films doped with CdTe NPs produced (A) in DIW and (B) in methanol at same parameters (E=100 mj, λ =1064 nm, F=6Hz and 300 pules)	88
4-10	EDX spectra taken onto the PVA films doped with CdTe NPs Produced) A) in DIW and (B) in methanol at same parameters (E=100 mj, λ =1064 nm, F=6Hz and 300 pules).	89
4-11	The absorbance spectra as a function to wavelength of CdTe NPs suspended in colloid solutions and produced (A) in DIW and (B) in methanol by laser ablation at (E=100 mj, λ =1064 nm, F=6Hz) and different laser shots (100, 200, 300) pulse	91
4-12	The absorbance spectra as a function to wavelength for the (A) PVA film in its pure state and PVA films doped with CdTe NPs which ablated in DIW and (B) in methanol with different laser shots	93
4-13	The transmittance spectra as a function to wavelength of CdTe NPs suspended in colloid solutions and produced (A) in DIW and (B) in methanol by laser ablation at The (E=100 mj, λ =1064 nm, F=6Hz) and different laser shots (100, 200, 300) pulse	95

4-14	The transmittance spectra as a function to wavelength for the (A) PVA film in its pure state, and PVA films doped with CdTe NPs which ablated in DIW and (B) in methanol with different laser shots	96
4-15	The reflectance curve as a function to wavelength of CdTe NPs suspended in colloid solutions and produced (A) in DIW and (B) in methanol by laser ablation at (E=100 mj, $\lambda=1064$ nm, F=6Hz) and different laser shots (100, 200, 300) pulse	97
4-16	The reflectance curves as a function to wavelength for the PVA films doped with CdTe NPs which ablated (A) in DIW and (B) in methanol with different laser shots	98
4-17	Absorption coefficient curve as a function to wavelength of CdTe NPs suspended in colloid solutions and produced (A) in DIW and (B) in methanol by laser ablation at (E=100 mj, $\lambda=1064$ nm, F=6Hz) and different laser shots (100, 200, 300) pulse	99
4-18	Refractive index curve as a function to wavelength of CdTe NPs suspended in colloid solutions and produced (A) in DIW and (B) in methanol by laser ablation at (E=100 mj, $\lambda=1064$ nm, F=6Hz) and different laser shots (100, 200, 300) pulse	100
4-19	Extinction coefficient curve as a function to wavelength of CdTe NPs suspended in colloid solutions and produced (A) in DIW and (B) in methanol by laser ablation at (E=100 mj, $\lambda=1064$ nm, F=6Hz) and different laser shots (100, 200, 300) pulse	101
4-20	Absorption coefficient curves as a function to wavelength for the PVA films doped with CdTe NPs which ablated (A) in DIW and (B) in methanol with different laser shots	102
4-21	Refractive index coefficient curves as a function to wavelength for the PVA films doped with CdTe NPs which ablated (A) in DIW and (B) in methanol with different laser shots	103
4-22	Extinction coefficient curves as a function to wavelength for the PVA films doped with CdTe NPs which ablated (A) in DIW and (B) in methanol with different laser shots	104
4-23	A plot of $\ln(\alpha h\nu)$ verses $\ln(h\nu - E_g)$ for colloidal CdTe NPs dissolved in DIW	104
4-24	$(\alpha h\nu)^2$ versus photon energy gap varies of colloidal CdTe NPs produced in (A) DIW and (B) methanol by laser ablation with laser shots (100, 200, 300) pulse	105

4-25	$(\alpha h\nu)^2$ versus photon energy gap varies of PVA/CdTe NPs films doped with colloidal CdTe NPs produced in (A) DIW and (B) methanol according to laser shots (100, 200, 300) pulse	106
4-26	The relation between real dielectric constant and wavelength of colloidal CdTe NPs produced in (A) DIW and (B) methanol by laser ablation with laser shots (100, 200, 300) pulse	108
4-27	The relation between imaginary of dielectric constant and wavelength of colloidal CdTe NPs produced in (A) DIW and (B) methanol by laser ablation with laser shots (100, 200, 300) pulse	109
4-28	The relation between optical conductivity and wavelength of colloidal CdTe NPs produced in (A) DIW and (B) methanol by laser ablation with laser shots (100, 200, 300) pulse	109
4-29	The relation between real dielectric constant and wavelength of PVA/CdTe NPs films doped with colloidal NPs produced in (A) DIW and (B) methanol according to laser shots (100, 200, 300) pulse	110
4-30	The relation between imaginary of dielectric constant and wavelength of PVA/CdTe NPs films doped with colloidal NPs produced in (A) DIW and (B) methanol according to laser shots (100, 200, 300) pulse	110
4-31	The relation between optical conductivity and wavelength of PVA/CdTe NPs films doped with colloidal NPs produced in (A) DIW and (B) methanol according to laser shots (100, 200, 300) pulse	111
4-32	The normalize transmittance curve as a function to position for the samples of colloidal solutions of CdTe NPs produced in (A) DIW and (B) pure methanol at (100, 200 300) pulse. Close aperture z-scan CW diode laser ($\lambda= 650\text{nm}$, $P= 50\text{Mw}$)	112
4-33	The normalize transmittance curve as a function to position for the samples of colloidal solutions of CdTe NPs generated in (A) DIW and (B) pure methanol at (100, 200 300) pulse. Open aperture z-scan with CW diode laser ($\lambda= 650\text{nm}$, $P= 50\text{Mw}$)	113
4-34	The relation between NLR index and the laser shots number applied to preparation of different colloid solutions of CdTe NPs produced in (A) DIW and (B) pure methanol	114
4-35	The relation between NLA coefficient and the laser shots number applied to preparation of different colloid solutions of CdTe NPs produced in (A) DIW and (B) pure methanol	115

4-36	The normalize transmittance curve as a function to position for PVA/CdTe NPs films prepared from addition of colloid solution of CdTe NPs produced in (A) DIW and (B) pure methanol, at (100, 200 300) pulse. Close aperture z-scan with CW diode laser ($\lambda= 650\text{nm}$, $P= 50\text{Mw}$)	117
4-37	The normalize transmittance curve as a function to position for PVA/CdTe NPs films prepared from addition of colloid solutions of CdTe NPs produced in (A) DIW and (B) pure methanol, at (100, 200 300) pulse. Open aperture z-scan with CW diode laser ($\lambda= 650\text{nm}$, $P= 50\text{mW}$)	118
4-38	The relation between NLR index and the laser shots number and the different laser shots, which is the control factor for the different concentrations of nanoparticles produced in (A) DIW and (B) pure methanol and added to the PVA films	119
4-39	The relation between NLA coefficient and the laser shots number and the different laser shots, which is the control factor for the different concentrations of nanoparticles produced in (A) DIW and (B) pure methanol and added to the PVA films	120
4-40	Optical limiting behavior of CdTe NPs produced in (A) DIW and (B) Methanol at different laser shots (100, 200, 300) pulse	122
4-41	Transmittance output of optical Limiter as Function of the Input power for CdTe NPs produced in (A) DIW and (B) methanol at different laser shots (100, 200, 300) pulse	123
4-42	Optical limiting behavior of PVA/ CdTe NPs films doped with different concentrations of CdTe NPs produced in (A) DIW and (B) methanol according to applied laser shots (100, 200, 300) pulse	124
4-43	Transmittance output of optical limiter as Function of the Input power of PVA/CdTe NPs films doped in two case of (A) DIW and (B) methanol at laser shots (100, 200, 300) pulse	125

Contents

NO.	Subject	Page
	Abstract	I
	List of Abbreviation	III
	List of Physical Symbols and Units	IV
	List of Tables	VI
	List of Figures	VII
	Contents	XIII
Chapter One: Introduction		
1.1	Nanotechnology	1
1.2	Nonlinear Optics	2
1.3	Semiconductor Nanomaterials	3
1.4	Cadmium Telluride Compound	6
1.5	Advance of Pulsed Laser Ablation in Liquids (PLAL)	8
1.6	Literatures Review	11
1.7	Aims of thesis	18
Chapter Two: Theoretical concepts		
2.1	Introduction	19
2.2	Polyvinyl Alcohol (PVA) Polymer	19
2.3	Nano-materials	20
2.4	Classification of nano-materials	21
2.4.1	Zero-dimensional nano-materials (0D)	21
2.4.1	One-dimensional nano-materials (1D)	21
2.4.2	Two-dimensional nano-materials (2D)	22
2.4.4	Three-dimensional nano-materials (3D)	22
2.5	Synthesis of Nanoparticles	23
2.5.1	Top down approach (Dispersion Methods)	23

2.5.2	Bottom up approach (Reduction Methods)	24
2.6	Laser ablation and Particle Formation	25
2.6.1	Laser-Induced Heating and Fusion	25
2.6.2	Explosive Boiling	26
2.6.3	Evaporation	26
2.6.4	Plasma Formation	27
2.6.5	Solid Peeling	27
2.6.6	Particle Ejection (Spallation)	28
2.6.7	Nucleation and Condensation	29
2.6.8	Coagulation and Agglomeration (Growth)	29
2.7	Influence of Laser Ablation Conditions on the Formation Efficiency of NPs by PLAL	30
2.7.1	Influence of physical parameters	31
2.7.1.1	Laser Energy	31
2.7.1.2	Ablation Time	31
2.7.1.3	Repetition rate and number of pulses	31
2.7.2	Influence of chemical parameters	32
2.7.2.1	Solvent	32
2.7.2.2	Solid target	33
2.8	Structural Properties of semiconductors	33
2.8.1	Lattice Constant (a)	34
2.8.2	Average Grain Size $(G. S)_{av}$	35
2.8.3	Dislocation Density and Strain	35
2.9	Optical properties of semiconductors	35
2.9.1	Transmittance	37
2.9.2	Absorbance	38
2.9.3	Reflectivity	38
2.9.4	Optical Energy Gap	38
2.9.5	Optical constants	40
2.9.5.1	Absorption Coefficient	40
2.9.5.2	Extinction Coefficient	41

2.9.5.3	Refractive Index	41
2.9.5.4	Dielectric Constant	42
2.9.5.5	Photoconductivity	43
2.10	Nonlinear optical properties	43
2.10.1	nonlinear refraction and nonlinear absorption	44
2.10.2	Saturation Absorption	45
2.10.3	Two Photon Absorption	45
2.10.4	Self-focusing and Self-defocusing	46
2.10.5	Third order nonlinear process	47
2.11	Z-Scan technique	48
2.11.1	Closed-aperture Z-scan Technique	49
2.11.2	Open-aperture Z-scan Technique	51
2.12	Nonlinear Optical Constants	51
2.12.1	Nonlinear Refractive (NLR) index	51
2.12.2	Nonlinear Absorption (NLA) Coefficient	52
2.13	Optical Limiting	53
Chapter Three: Experimental Part		
3.1	Introduction	55
3.2	Preparation of material and solvents used	56
3.2.1	CdTe material	56
3.2.2	PVA Polymer	56
3.2.3	Solvents	56
3.2.3.1	Distilled water (DIW)	56
3.2.3.2	Methanol	57
3.3	Preparation of glass-substrates	57
3.4	Preparation of work system	58
3.4.1	Nd-YAG Laser Device	59
3.4.2	Semiconductor Laser Device	59
3.5	General Experimental Process	60

3.5.1	Preparation of colloidal solutions of NPs & PVA/CdTe NPs films	61
3.5.2	General Experimental Process of Z-scan Technique	62
3.5.3	General Experimental Process of Optical Limiting:	63
3.6	Measurement Devices	64
3.6.1	UV-Visible Spectrophotometer	64
3.6.2	Thin Films Thickness Measurement Device	65
3.6.3	X-ray Diffraction Device	65
3.6.4	Scanning Electron Microscopy (SEM)	66
3.6.5	Energy Dispersive X-ray spectroscopy (EDX)	67
3.6.6	Atomic Force Microscope (AFM)	68
Chapter Four: Results and Discussions		
4.1	Introduction	69
4.2	Investigations of Structure Properties	69
4.2.1	XRD Analyzes	69
4.2.2	AFM Analyzes	75
4.2.3	SEM and EDX Analyzes	84
4.3	Linear Optical Properties	90
4.3.1	Absorbance	90
4.3.2	Transmittance	94
4.3.3	Reflectance	96
4.3.4	Absorption coefficient & Refractive index and Extinction coefficient	98
4.3.5	Optical Energy Gap	104
4.3.6	Real and Imaginary Part of Dielectric Constant & Optical conductivity	107
4.4	Nonlinear Optical Properties	111
4.4.1	Nonlinear optical properties of colloidal solutions of CdTe NPs	111
4.4.2	Nonlinear optical properties of PVA/CdTe NPs films	116
4.4.3	Optical limiting	121

	Chapter Five : Conclusions and Future Work	
5.1	Conclusions	128
5.2	Suggestion of future works	129
	References	130

الخلاصة

تقدم هذه الرسالة طرق سهلة وسريعة وبخطوة واحدة فعالة لإعداد وتوصيف الخواص البصرية الخطية واللاخطية لجسيمات نانوية شبه الموصلة النقية والمستقرة ذات معدل استئصال عالي وبحجم وخصائص مسيطر عليها مع تراكيز عالية ، وغير سامة او ملوثة.

اولا: حضرت الجسيمات النانوية العالقة في المحاليل الغروية باستخدام ليزر Nd-YAG (Q-switched) النبضي بطريقة التبخير الانفجاري لقطعة صلبة فائقة النقاوة من مركب تيلوريد الكاديوم كهدف مغمورة في الماء المقطر او محلول اخر مثل الميثانول ذو النقاوة العالية. تم استخدام معلمات التحضير بواسطة الليزر النبضي والتي اثبتت كفاءة جيدة في توليد الجسيمات النانوية بطريقة التبخير الانفجاري (PLAL)، وهذه المعلمات هي عدد نبضات الليزر كانت (100، 200، 300) نبضة. طاقة الليزر والطول الموجي كانتا ثابتة عند 100mj و 1064nm، على التوالي. معدل التكرار و امد النبضة كانتا 6Hz و 10ns، على التوالي. علاوة على ذلك، كانت كمية السائل الموضوع في الاناء الزجاجي (2mL).

ثانيا: حضرت أفلام من البولي فنائل الكحول (PVA) المشوبة بالمحاليل الغروية الحاوية على تراكيز مختلفة من الجسيمات النانوية حسب أعدادها وفقا لعدد النبضات المختلفة، حيث حضرت الاغشية بطريقة الصب على قواعد زجاجية وبسمك (10µm).

بينت قياسات حيود الاشعة السينية لجميع العينات المعدة ان جسيمات CdTe النانوية المرسبة على الزجاج ذات تركيب متعدد التبلور بطور مكعب بأعلى قمة عند الزاوية 23.79° وفقا للمستوى (111)، بثابت شبكية (a=6.59nm) وبحجوم حبيبية متزايدة نسبيا للجسيمات النانوية. كذلك بينت قياسات XRD لأغشية PVA المشوبة بالجسيمات النانوية حصول انخفاض في قمم الشدة ونقصان في حدتها مع اختفاء البعض إضافة لحصول انخفاض في الحجم الحبيبية للجسيمات النانوية وتزايد في قيم المطاوعة وكثافة الانخلاع.

بينت نتائج فحوصات المجهر الإلكتروني الماسح (SEM) لجسيمات تيلوريد الكاديوم النانوية المرسبة على الزجاج ان العينات المعدة تتكون من هياكل كروية غير منتظمة الشكل تتشكل على سطح الغشاء مع وجود عيوب خطية لأغشية المركب (CdTe) بينما يحصل تغير طفيف في أشكال واحجام الحبيبات بأشكال كروية اكثر تجانسا بعد تشويبيها في البوليمر. اثبتت نتائج

فحوصات EDX ان المحاليل الغروية المحظرة ذات نقاوة عالية وتحتوي على عنصري Cd و Te بنسب عالية فظلا عن بقائها بعد الخلط مع البوليمر في أغشية PVA المحظرة.

بينت دراسة طبوغرافية السطح للمواد النانوية المرسبة على الزجاج باستخدام مجهر القوة الذرية (AFM) حصول تفاوت نسبي قليل في معدل اقطار الجسيمات النانوية وخشونة السطح اذا تزداد مع زيادة عدد النبضات الليزر، اذ تم الحصول على اقل قطر للجسيمات النانوية المحظرة في محلول الميثانول. في حين تنخفض اقطار الجسيمات النانوية وخشونة السطح بعد تشويبها في البوليمر.

تم دراسة تأثير البيئة السائلة وعدد النبضات على الخواص البصرية للجسيمات النانوية الغروية ولأغشية PVA لمشوبة بالجسيمات النانوية بواسطة جهاز مطياف الاشعة فوق البنفسجية والمرئية، اذ بينت النتائج بأن الامتصاصية للمحاليل الغروية وللأغشية المشوبة بالجسيمات النانوية تزداد بزيادة عدد النبضات، وحصول تغيير لقيم المعلمات البصرية (النفاذية ، الانعكاسية ، فجوة الطاقة البصرية، معامل الامتصاص، معامل الانكسار، معامل الاضمحلال، الجزء الحقيقي والخيالي لثابت العزل الكهربائي، التوصيلية البصرية).

كذلك تم دراسة تأثير الوسط والتركيز لجسيمات CdTe النانوية واغشية PVA/CdTe النانوية على الخصائص البصرية اللاخطية والمحدد البصري بتقنية المسح على المحور الثالث باستخدام ليزر الداويد المستمر ذو الطول الموجي(650nm)، وبقدرة خارجة (50mW). اذ بينت النتائج ان جميع العينات المعدة تضمنت معامل انكسار لا خطي سالب بمعنى حصول ظاهرة اللاتركيز الذاتي وظاهرة امتصاص ثنائي الفوتون. ووجد معامل الانكسار اللاخطي يزداد مع زيادة التركيز، بينما لوحظ ان معامل الامتصاص اللاخطي يقل مع زيادة التركيز لجميع الحالات. كذلك تمت المقارنة بين جميع النماذج المعدة في حالة المحاليل الغروية واغشية PVA المطعمة بالجسيمات النانوية من حيث عتبة المحدد وسعة المحدد فوجد إنها تمتلك خواص محدد بصري و كفاءة افضل بزيادة تراكيز الجسيمات النانوية في كلا من المحاليل والاغشية. أثبتت النتائج التي تم الحصول عليها لجميع الحالات أنه يمكن استخدام هذه النماذج في تطبيقات واسعة من الأجهزة البصرية اللاخطية.



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