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Preparation and Characterization of Teo_2 Nano particles by Pulsed Laser Ablation in Water

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ABSTRACT

Tellurium dioxide (TeO_2) nanoparticles were synthesized directly by pulsed laser ablation using Nd:YAG, λ=1064nm laser in pure water. The AFM and XRD measurements, in combination with FTIR and UV–Vis spectroscopy have been employed for the characterization of the prepared samples. The effects of operating parameters on nanoparticles composition, production rate and size were also studied. The XRD measurements revealed crystallization structure of TeO_2 nanoparticles. The particle diameter by use of Scherer's equation was calculated to be about 28. nm and confirmed by AFM measurements. The UV–vis spectrum of the colloidal nanoparticles shows maximum absorbance around the UV region, indicating the formation of TeO_2 nanoparticles, which confirmed by FTIR.

Keywords: Pulsed Laser Ablation, Nano Particles, Tellurium Nano-Particles.

تحضير ودراسة خصائص جسيمات ثنائي اوكسيد التليريوم النانوية بواسطة القشط بليزر نبضي بالوسط المائي

الخلاصة

جسيمات ثنائي اوكسيد التليريوم TeO_2 النانوية تم تحضيرها بواسطة تشعيع معدن التليريوم النقي بليزر النديميوم ياك النبضي ذو الطول الموجي 1064 nm داخل الماء المقطر. تم تشخيص الجسيمات المتولدة بواسطة مجهر القوى الذرية AFM وحيود الاشعة السينية XRD ومطياف FTIR ومطياف المنطقة المرئية وفوق البنفسجية UV-Vis . تأثيرات عوامل التحضير وكفاءة التوليد وحجم الجسيمات المتولدة تمت دراستها. قياسات حيود الاشعة السينية توحي توليد التركيب البلوري لجسيمات TeO_2 النانوية. قطر الجسيمات النانوية تم حسابها بواسطة معادلة شيرر وكانت بحدود 28 nm وهي تتفق مع قياسات ال AFM. طيف الامتصاص للعوالق النانوية اظهرت قيمة أمتصاص عظمى في المنطقة الفوق بنفسجية والتي تدل على توليد جسيمات TeO_2 النانوية والتي اثبتت بواسطة قياسات ال FTIR ايضا.

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INTRODUCTION

Pulsed laser ablation in liquid media (PLAL) is a promising technique for the controlled fabrication of nanomaterials via rapid reactive quenching of ablated species at the interface between the plasma and liquid. PLAL is a versatile technique for preparing various kinds of nanoparticles (NPs) such as noble metals, alloys, oxides and semiconductors [1, 2]. Compared to conventional wet chemical synthesis, pulsed laser ablation in liquids affords the synthesis of pure nanoparticles colloids without impurities caused by chemical precursors or preservatives and a great variability of the single step process applicable to diverse metals and alloys, ceramics, and semiconductors in various liquids. Furthermore, chemicals like surfactants or ligands can be directly added to the liquid before laser ablation as in situ conjugation agent in order to control parameters like particle size or synthesize nanoparticle-conjugates with targeted properties like bioconjugates [3]. Tellurium thin films have been widely used as gas sensors at room temperature for the detection of nitrogen dioxide and ammonia and as cooling devices [4]. Nanoparticles have been prepared by a wide variety of techniques such as pulsed laser deposition [5], chemical reduction [6], photoreduction [7], electrochemical reduction [8]...etc. Among them, the pulsed laser ablation in liquid medium has become an increasingly popular top-down approach [9] for producing nanoparticles.

Tellurium oxide thin films have been prepared by various techniques such as reactive sputtering [10], dip-coating [11] and vapor deposition [12]. However, so far there are a few works reported in literature relating to the synthesis of α-TeO_2 nano and microstructures [13–19]. Jiang et al. [13] fabricated tellurium oxide nanorods by laser ablation of elemental tellurium on the glass substrate in a hot air atmosphere. Huriet et al. [14] synthesized microcrystals of TeO_2 by hydrolysis of tellurium isopropoxide in the presence of tetra alkyl ammonium bromide solution. Qin et al. [15] prepared TeO_2 nanoparticles in acid medium, such as gallic acid or acetum, at room temperature. Liu et al. [16] and Siciliano et al. [17] reported the synthesis of TeO_2 nanowires through thermal evaporation of Te metal in air. Filippo et al. [18] and Kim et al. [19] achieved the growth of α-TeO_2 beaded microwires and branched nanowires, respectively, through thermal evaporation method using Te as source material.

The class of Te^{IV} containing compounds, which includes tellurium dioxide (TeO_2) either in amorphous or crystalline phase, exhibits remarkable dielectric, piezoelectric, optic and electro-acoustic properties, each of them of great interest for fundamental science and technology. Potential applications of TeO_2-based glasses are directed toward optical fibre or non-linear optical devices. TeO_2 single crystals are a very promising material for use in ultrasonic generators [20] and especially in acousto-optic devices [21]. Such components request large single crystals with high crystalline and optical quality, high homogeneity, low light absorption and scattering and high optical power capability. Because of these specific demands, a better understanding of the growing process is very important. Recently, investigations on the growth of TeO_2 single crystals were made and the effect of the growing conditions on the quality of the obtained crystals was studied [22].

EXPERIMENTAL PROCEDURES OF PLAL AND NANO MATERIAL PREPARATION

Tellurium nanoparticles were synthesized by laser ablation process, which is a combination of focused pulsed laser ablation of a piece of tellurium metal plates (purity: 99.999%) placed on the bottom of quartz vessel containing 3ml of double distilled deionised water DDDW which prepared by Elgastat Deioniser type (B.113) with conductivity 2×10-6 $(\Omega\ cm)^{-1}$.The Nd-YAG laser (type HUAFEI) of 1064 nm at energy (750mJ) per pulse, with a positive lens having a focal length of 110 mm, was utilized as an ablation source.. The effective spot size of the laser beam on the surface of the metal plate was 1.27 mm. The number of laser shots applied for the metal target was 20 pulses. Absorbance spectra of the nanoparticles solution (placed on the quartz cell) was measured by UV-visible (UV-VIS) double beam spectrophotometer CECIL, C. 7200 (France). Other optical properties such as energy band gap Eg (eV) also calculated. The colloidal solution was made to vibrate for 10 min by ultrasonic vibrator in order to get homogeneity of the product, and then dropped on the glass substrate, dried in an oven at $60C^{o}$ temperature in order to convert TeO_2 nanoparticles colloidal to nanoparticles thin films. The average particle size and amount of aggregation of NPs were characterized with atomic force microscope (AFM) AA300 scanning probe microscope Angstrom Advanced Inc. Figure (1) shows the experimental setup of PLAL system and Figure (2) displays the photograph of TeO_2 NPs prepared by laser ablation method. The dark black colloidal solution of TeO_2 is obtained after laser irradiation of 20 pulses.

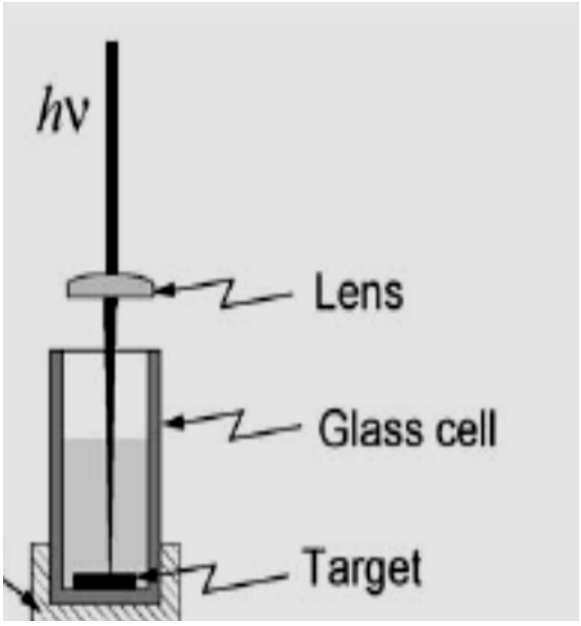

Figure (1) The experimental setup of PLAL system.

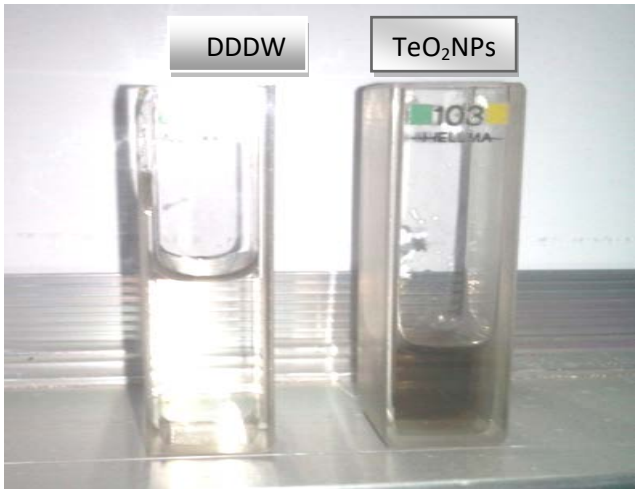

Figure (2) Photograph of prepared colloidal TeO_2 Nanoparticles.

RESULTS AND DISCUSSION

Figure (3) shows UV–visible absorption spectra of TeO_2 NPs, immediately after ablation. The absorption spectrum is increases rapidly centered at about 210 nm with a long tail towards longer wavelength. This peak is the characteristic of TeO_2 formation. The tail may be due to the scattering of a range of particle sizes and some type Urpach effect due to intergrain depletion regions (Gondal et al. 2009)[23]. .The variation of $(\alpha h\upsilon)^2$ with photon energy ($h\upsilon$) is depicted in Figure (4). The optical band gap Eg of TeO_2 NPs is determined from extrapolating the linear part of $(\alpha h\upsilon)^2$ $h\upsilon$ plot on the X-axis. The optical gap found to be 5.8 eV . The shift of the exciton peak with particle size is attributed to quantum confinement due to induced energy gap variation by Brus et. al .[24]. The spectral properties of semiconductor have been shown to vary with quantization effects. The value of band gap energy (ΔE) varies with the radius of the particles (d) [25].

$$\Delta E=\left(\frac{\hbar}{2\ me*}\right)\left(\frac{\pi^2}{d^2}\right) \qquad \ldots (1)$$

Where ΔE (energy shift or optical gap shift) with the respect to bulk band gap (3.7 ev) and d is the particle size , h the Planck's constant and me* is the electron reduced mass thus with a decrease in particle size, the energy of optical transition increases as shown in Figure (4).

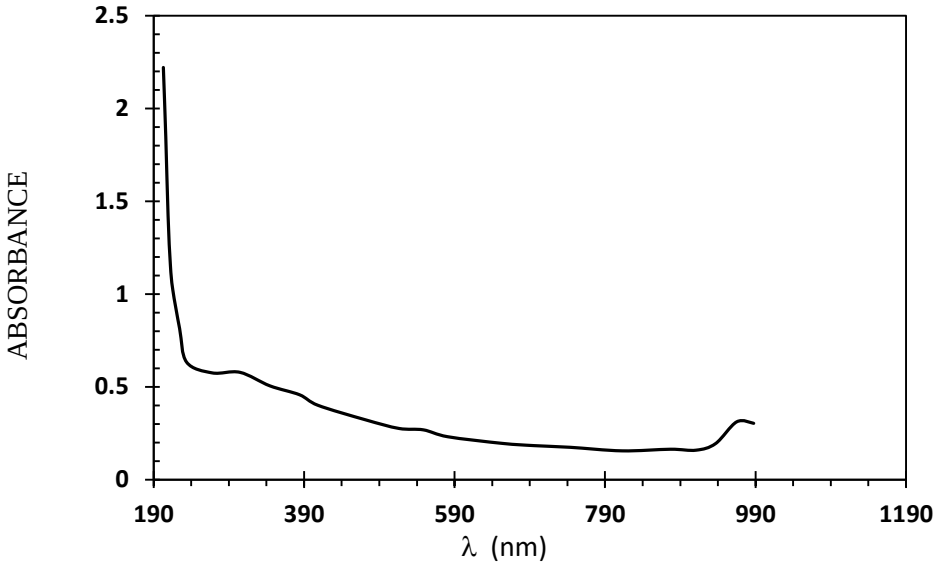

Figure (3) Absorption spectrum of TeO_2 NPs.

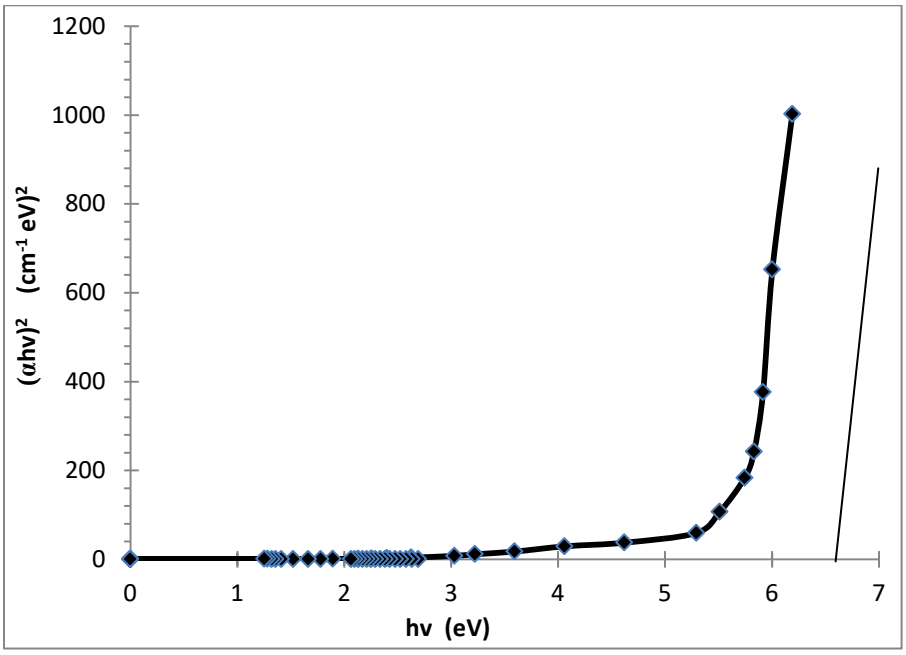

Figure (4) $(\alpha h\upsilon)^2$ versus photon energy plot for ablated with energy of 750mJ and number of pulses of 20 .

The phase and purity of the NPs were further examined by X-ray diffraction shows in Figure (5). All of the reflections in Fig. 5 can be indexed on a tetragonal α-TeO_2 with lattice constants of a = b = 0.480 nm and c = 0.761 nm (JCPDS No. 78-1713). [21, 22]. The XRD measurements revealed crystallization structure of TeO_2 nanoparticles. The crystallite size (grain size) (D) were calculated using the Scherrer formula from the full-width at half-maximum (FWHM) (Δ)(Red) [26] with other parameters are listed in Table (1).

$$D = \left(\frac{0.94\lambda}{\Delta \cos\theta} \right) \quad \ldots (2)$$

Where λ is wavelength of the X-rays and θ is Bragg angle. In this work, X-ray diffraction measurements have been done according to the ASTM (American Society of Testing Materials) cards, using Philips PW 1050 X-ray diffractometer of 1.54 Å from Cu-kα.

Table (1) shows TeO_2NP_S parameters.

Symbol	2θ(deg)	$d_{XRD(nm)}$	FWHM(deg)	FWHM(Red)	Grain size D(Å)	Grain size D(nm)
TeO_2	27.93	3.190	0.3102	0.0054	280	28

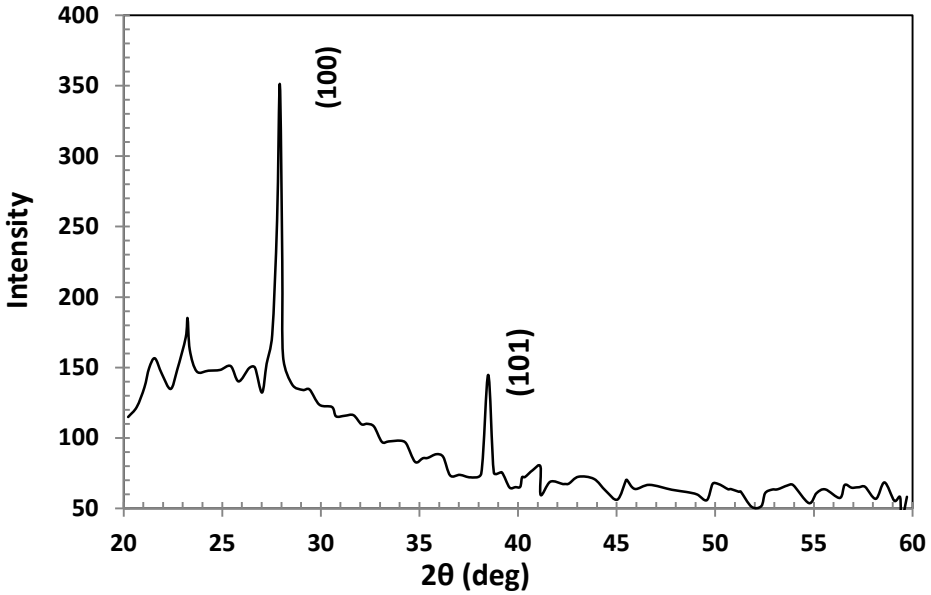

Figure (5) XRD analysis of the Tellurium oxide, TeO_2 **nanoparticles .**

FTIR spectroscopy was performed to analyze the functional organic groups attached to the surface of the Te NPs. Figure (6) shows a FTIR spectrum of nanotellurium oxide with some typical absorption bands; such as the bands centered at around 474.40cm^{-1} are assigned to the stretching vibrations of Te-O-Te linkages [27]. The bands centered at around 690cm^{-1} are originated from vibration of the continuous networks composed of [TeO_4] tetragonal bipyramids and the bands centered at around 710cm^{-1} are contributed to [TeO_{3+1}] and [TeO_3] structural units [27]. The strong absorption at 1672.28 cm^{-1} and 1097.5cm^{-1} that were correspond to carbonyl (C=O) and ester (COO) stretching vibrations respectively [22]. The absorption band at 2358 cm^{-1} was related to hydrocarbon (C–H) stretching vibrations. Three peaks at 1469.76, 1097.5 and 516.92 cm^{-1} were also related to ethyl group bending vibrations [22].Overall, it was concluded that an ester ketone residue (-CO-O) exists on the surface of Te nanoparticles .

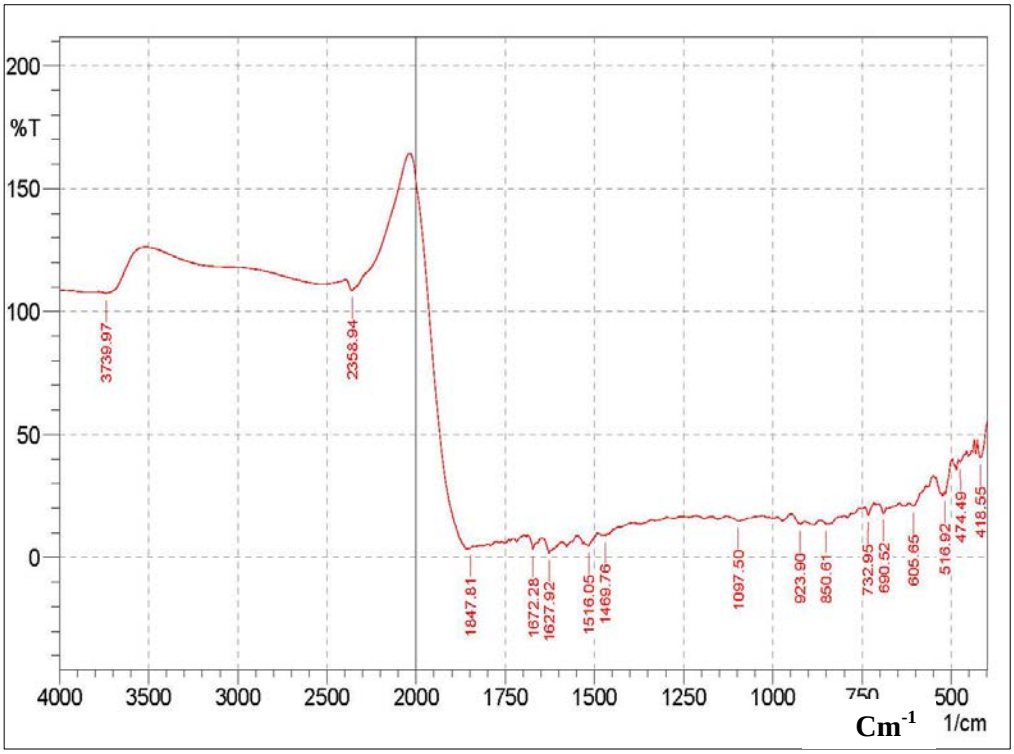

Figure (6) FTIR spectrum of the extracted TeO_2 NPs.

The atomic force microscope (AFM) with two and three dimensions images of tellurium oxide nanoparticals are presented in Figure (7). It's clear from figure that thin film consist of TeO_2 nanoparticales with average diameter of 47.21 nm are observed over the entire surface, as shown in the inset. The 3-dimensional (3D) AFM image of material nanopartical in which the irregular and randomly distributed nanoparticals TeO_2 over the entire surface can be seen with a maximum value of 18 nm exhibits morphology with a root-mean-square (RMS) roughness 1.82 nm.

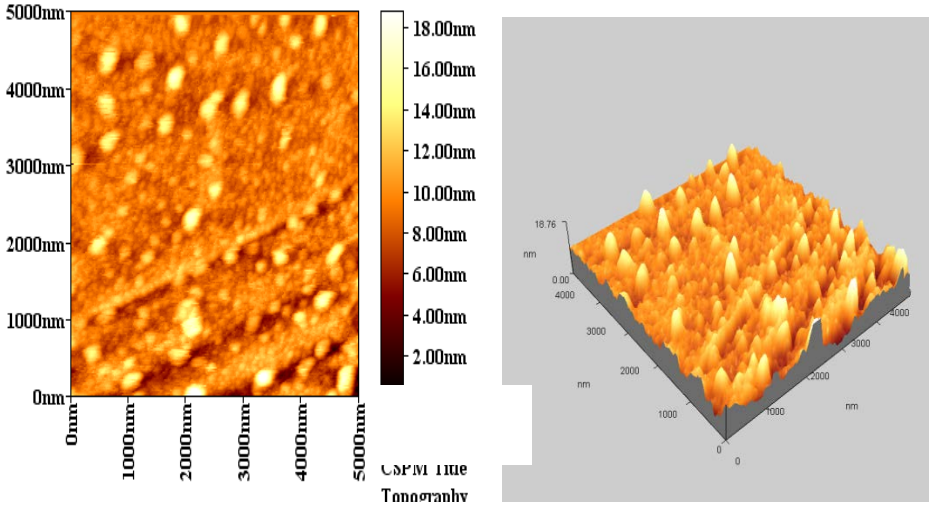

Figure (7) AFM images of TeO_2nanoparticals prepared by laser energy of 750 mJ .

CONCLUSIONS

In summary, we successfully demonstrated the synthesis of high purity TeO $_2$NPs colloid at room temperature by Nd:YAG laser ablation of Te target in water. The UV–vis spectrum of the colloidal nanoparticles shows maximum absorbance around the UV region. From AFM measurement we found the that the average size of NPs is about 47.21 nm with a root-mean-square (RMS) roughness of 1.82 nm .The particle diameter by use of Scherer's equation was calculated to be about 28 nm and confirmed by AFM measurements .From XRD measurement all peak can be indexed on a tetragonal α-TeO_2 with lattice constants of a = b = 0.480 nm and c = 0.761 nm ,which is in a good agreement with literatures .

REFERENCES

[1]. Takeshi Sasaki ⁎, Yoshiki Shimizu, Naoto Koshizaki "Preparation of metal oxide-based nanomaterials using nanosecond pulsed laser ablation in liquids" Journal of Photochemistry and Photobiology A: Chemistry 182, 335–341 (2006).

[2]. Thareja *, R.K. Shobha Shukla" Synthesis and characterization of zinc oxide nanoparticles by laser ablation of zinc in liquid" Applied Surface Science 253, 8889–8895 (2007).

[3].Philipp Wagener, Andreas Schwenke, Boris N. Chichkov, and Stephan Barcikowski*" Pulsed Laser Ablation of Zinc in Tetrahydrofuran: By passing the Cavitation Bubble" *J. Phys. Chem. C* 114, 7618–7625(2010).

[4].W.Phaengam[1,a],V.Kosalathip[1,b],T.kumpeerapun[1,c],P.Limsuwan1,d,andA.Dauscher[2,e]"preparationand characterization of Tellurium Nano-particles by long pulsed laser ablation "Advanced Materials research vol.214, PP202-206. (2011)

[5]. Donnelly, T. S. Krishnamurthy, K. Carney, N. McEvoy, J.G. Lunney (Pulsed laser deposition of nanoparticle films of Au) Applied Surface Science 254, 1303–1306 (2007).

[6]. Qiao,C. Wu, X. J. Chen, H. Wang, F. Tan, S. Li (A novel chemical route to prepare ZnO nanoparticles) Materials Letters 60, 1828–1832 (2006).

[7]. Jia,H. J. Zeng, W. Song, J. An, B. Zhao (Preparation of silver nanoparticles by photo-reduction for surface-enhanced Raman scattering) Thin Solid Films 496, 281–287(2006).

[8]. Lim, P.Y. R.S. Liu, P.L. She,C.F. Hung, H.C. Shih (Synthesis of Ag nanospheres particles in ethylene glycol by electrochemical-assisted polyol process) Chemical Physics Letters 420304–308, (2006).

[9]. Sylvestre, J. A. V. Kabashin, E. Sacher, M. Meunier, J. T. Luong (Stabilization and Size Control of Gold Nanoparticles during Laser Ablation in Aqueous Cyclodextrins) J. Am. chem. soc. 126, 7176-7177 (2004).

[10]. Nayak, R. V. Gupta, A.L. Dawar, K. Sreenivas," Optical wave guiding in amorphous tellurium oxide thin films", Thin Solid Films 445, 118–126 (2003).

[11]. Lecomte, A. F. Bamiere, S. Coste, P. Thomas, J.C. Champarnaud-Mesjard, Sol–gel processing of TeO_2 thin films from citric acid stabilized tellurium isopropoxide precursor, Journal of the European Ceramic Society 27, 1151–1158 (2007).

[12]. Arshak, K. O. Korostynska, Gamma radiation dosimetry using tellurium dioxide thin film structures, Sensors 2 ,347–355 (2002).

[13]. Jiang, Z.Y. Z.X. Xie, X.H. Zhang, S.Y. Xie, R.B. Huang, L.S. Zheng, Synthesis of α-tellurium dioxide nanorods from elemental tellurium by laser ablation, Inorganic Chemistry Communications 7, 179–181 (2004).

[14]. Huriet,A. S. Daniele, L.G. Hubert-Pfalzgraf, Effect of titanium additives on the growth of tellurium dioxide crystals in a sol–gel process, Materials Letters 59, 2379–2382 (2005)

[15]. Qin, B. Y. Bai, Y. Zhou, J. Liu, X. Xie, W. Zheng, Structure and characterization of TeO2 nanoparticles prepared in acid medium, Materials Letters 63, 1949–1951 (2009)

[16]. Liu, Z. T. Yamazaki, Y. Shen, T. Kikuta, N. Nakatani, Synthesis and characterization of TeO2 nanowires, Japanese Journal of Applied Physics 47, 771–774 (2008).

[17]. Siciliano,T. A. Tepore, G. Micocci, A. Genga, M. Siciliano, E. Filippo," Transition from n- to p-type electrical conductivity induced by ethanol adsorption on α-tellurium dioxide nanowires", Sensors and Actuators B 138, 207–213 (2009).

[18]. Filippo, E. G. Micocci, A. Tepore, T. Siciliano, Fabrication of α-TeO2 smooth and beaded microwires by thermal evaporation method, Journal of Crystal Growth" 336, 101–105. (2011).

[19]. Kim, S.S. J.Y. Park, S.W. Choi, H.G. Na, J.C. n Yang, D.S. Kwak, H.J. Nam, C.K. Hwangbo, H.W. Kim, Drastic change in shape of tetragonal TeO2 nanowires and their application to transparent chemical gas sensors, Applied Surface Science 258, 501–506 (2011).

[20]. Neamţu, C. Al. Darabonta, E. Surducan, Gh. Borodi"Crystal growth and electrical properties of TeO_2 single crystal "Journal of Optoelectronics and Advanced Materials Vol. 2, No. 5, p. 487-492(2000).

[21]. Filippoa , E. 1, T. Siciliano a,1, A. Gengab, G. Micoccia, M. Siciliano b, M. Teporea" Formation of α-TeO_2 pearl-like microwires templated on porous microtubes through thermal oxidation of Te microtubes" Applied Surface Science *265, 329– 333 (2013).*

[22]. Bijan Zare a, Mohammad Ali Faramarzi a, Zargham Sepehrizadeh a, Mojtaba Shakibaie b,Sassan Rezaie c, Ahmad Reza Shahverdi a,*" Biosynthesis and recovery of rod-shaped tellurium nanoparticles and their bactericidal activities" Materials Research Bulletin 47, 3719–3725 (2012).

[23]. Gondal M, Drmosh Q, Yamani Z, Saleh T "Synthesize of ZnO2 nanoparticles by laser ablation in liquid and their annealing transformation into ZnO nanoparticles". Appl Surf Sci Volume 256, Issue 1, 2009, Pages 298‑304 .

[24]. Bouvy and B. L.Suy C. " ZnO@Porous Media, Their PL and Laser Effect "J. Mater. Sci. Technol., vol.24 no.4, 2008.

[25]. Thareja , R.K. Shobha Shukla" Synthesis and characterization of zinc oxide nanoparticles by laser ablation of zinc in liquid" Applied Surface Science , no.253, P: 8889–8895, 2007.

[26]. Lalitha, S. R. Sathyamoorthy, S. Senthilarasu,A. Subbarayan, K. Natarajan, " Characterization of CdTe thin film – dependence of structural and optical properties on temperature and thickness " , Sol. Energy Mater. Sol. Cells 82 PP. 187-199, (2004).

[27]. Simona Rada1, ☋, Adriana Dehelean1,2, and Eugen Culea1" FTIR, Raman, UV-VIS spectroscopy and DFT investigations on the structure of the iron-lead-tellurate glasses" Journal of Molecular Modeling 17, 8 (2010) 2103-2111 .