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Synthesis and nonlinear optical properties of Zn doped TiO_2 nano-colloids

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ABSTRACT

This article summarizes investigations on nonlinear optical properties of Zn doped TiO_2 nano-colloidal suspension under pulsed excitation. Zn (1, 2 and 5 wt%) doped TiO_2 nanoparticles (NPs) have been synthesized using sol-gel method. Ultraviolet–visible studies revealed maximum blue shifting of absorption wavelength due to quantum size effect for undoped TiO_2 NPs. Zn doped TiO_2 NPs show slight increase in the absorption wavelength attesting the increase in the particle size with Zn doping. X-ray diffraction pattern confirms the presence of anatase phase of crystalline TiO_2 with average crystallite size of 6 nm. FESEM and TEM micrographs attest formation of uniform spherical like TiO_2 NPs. Nonlinear optical properties of these nano-colloids have been studied using open and closed aperture Z-scan technique employing the fundamental at 1064 nm of a 7ns mode-locked Nd-YAG laser operating at 10 Hz. 5 wt% Zn doped TiO_2 nano-colloids show enhanced nonliear refractive and absorption coefficients.

1. Introduction

Titanium dioxide (TiO_2) is high band gap (E_g > 3.2eV) transition metal oxide semiconductor having low production cost, high chemical stability and is attracting increasing interests due to its applications in high efficient photo catalyst, gas sensors, self-cleaning windows, anti-reflection coatings for photovoltaic cells, solar cells, luminescent materials etc. [1–5]. Bulk TiO_2 is used as a white pigment in paints, coatings and plastic. Nano TiO_2 has tremendous applications in foodstuffs and cosmetics [6]. Among three polymorphic crystalline phases of TiO_2 (anatase, rutile and brrokite), anatase with tetragonal crystal structure is predominant because of its high activity in photocatalysis [7].

Properties of technologically importance e.g. photo catalytic efficiency can be improved on doping. This includes doping with metal ions, dye photosensitization, deposition of noble metals, etc. [8–10].

Nanostructured semiconductors are also well-known for their linear and nonlinear optical (NLO) properties and may found potential applications in photonic devices, field emission display panels, optoelectronic devices, gas sensors, medicine, etc [11–14]. Second harmonic generation (SHG) is the property of non-centrosymmetric materials, however nanostructured phase show SHG because of breaking of inversion symmetry at the surface [15–18]. Third order nonlinear optical effects are enhanced in semiconducting nanostructured materials due to quantum confinement, high polarizibility and interfacial effects [19]. In our previous works [20–25], many semiconductor NPs and nanocomposites were investigated for their NLO properties. Interests still remain in this area in order to obtain material with high NLO coefficients. NLO properties of TiO_2 have been studied by many authors [26–28]. L Irimpan et al. obtained enhanced nonlinear absorption and refraction in ZnO-TiO2 nanocomposites due to increased exciton oscillator strength [29] Several authors have studied enhancement in NLO properties due to doping with Au, Ag, graphene oxide, etc [30–32].

In this paper, we report synthesis of Zn doped TiO_2 NPs by sol-gel method. As synthesized Zn-TiO_2 NPs powder was calcined at 500 °C for 2 h. Zn-TiO_2 NPs were characterized by X-ray diffraction (XRD) technique for crystal information and particle size determination. Morphological studies were carried out using field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Linear optical properties were investigated using ultraviolet–visible (UV–vis) spectroscopy. Third order NLO properties of Zn-TiO_2 colloids were studied using single beam Z-scan technique under pulsed excitation of Nd-YAG laser at 1064 nm. The results are presented here.

2. Experimental

2.1. Materials and methods

All chemicals used in this reaction were of analytical reagent (AR)

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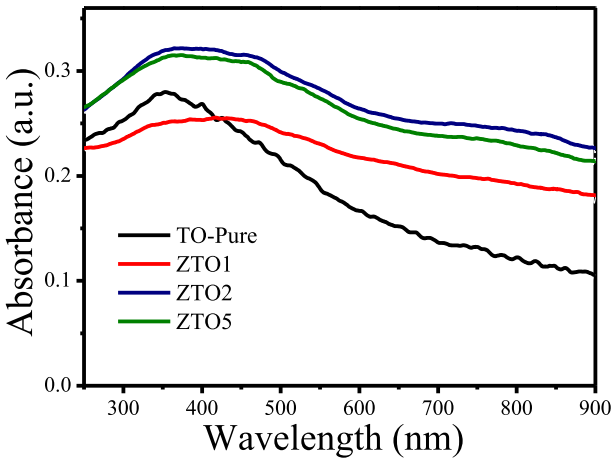

Fig. 1. UV–vis absorption spectra of pure and Zn doped TiO_2 NPs.

grade and were used as received without further purification. Titanium tetra isopropoxide (TTIP) and ethanol were purchased from Sigma Aldrich, USA. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$ 99.99%) was purchased from SD Fine Chemicals, India.

Powder samples of all NPs have been characterized by XRD technique using Rigaku diffractometer, MiniFlex II with nickel filtered CuK_α radiations (λ = 1.5406 Å), field emission scanning electron microscopy (FE-SEM) using field emission scanning electron microscope, S-4800, Hitachi, Japan. Zn doped TiO_2 NPs have been characterized by transmission electron microscopy (TEM) using JEM-2100 HR-TEM, Make-JEOL, Japan. Linear optical studies have been performed on ultraviolet–visible (UV–vis) spectrophotometer (BLK-C-SR, Stellarnet, USA) in the wavelength range 190–900 nm. Z-scan technique as developed by Bahae et al. [33,34] employing the fundamental at 1064 nm of a 7ns mode-locked Nd-YAG laser (Innolas spitlight compact 400 laser, USA) operating at 10 Hz has been utilized for NLO characterizations. The sample was translated along z-axis using microcontroller motorized linear translation stage (Holmarc, India) having resolution of 10 μm.

Table 1
Average particle size and band gaps obtained from XRD, TEM and UV–vis data.

Sample	Particle size (nm)			Band gap (eV)
	XRD	TEM	EMA model	
TiO_2-pure			2.6	3.62
ZTO1	6		3	3.53
ZTO2			3.3	3.45
ZTO5		7	3.8	3.37

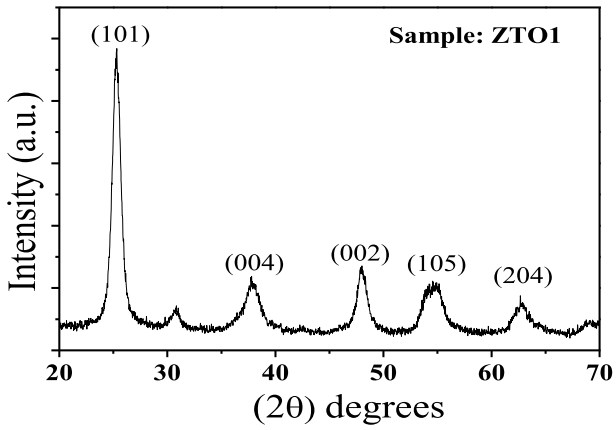

Fig. 3. XRD pattern of 1% Zn doped TiO_2 NPs.

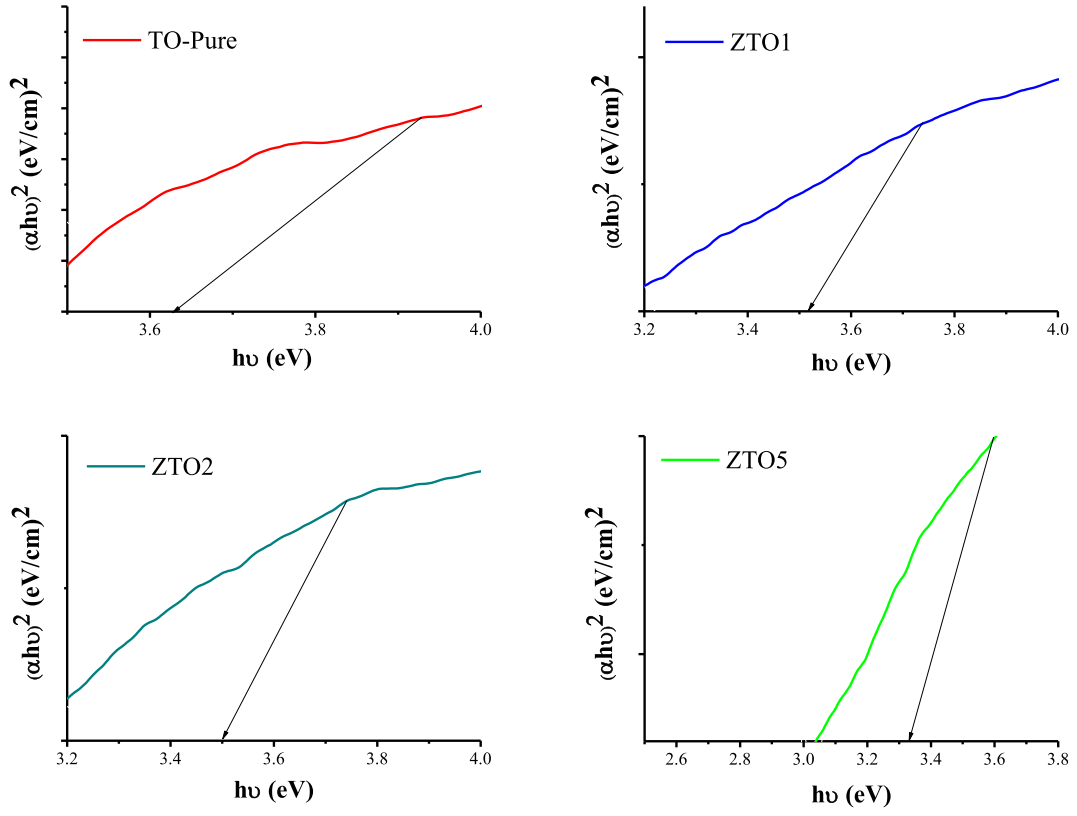

Fig. 2. Tauc's plots for pure and Zn doped TiO_2 NPs.