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Controlling the nonlinear absorption characteristics of TiO_2/carbon nanocomposites on films

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ABSTRACT

In this study, nonlinear and saturable absorption behaviors of nanocomposite TiO_2/carbon based materials in PMMA were investigated. Transparent thin films of TiO_2, HC/TiO_2, CNT/TiO_2, CNT/TiO_2-Pt nanocomposites were synthesized by spin coating. Linear absorption measurements indicate blueshift in energy due to a quantum confinement effect. Nonlinear optical absorption characteristics of the composite films were investigated using open aperture Z-scan technique with at the same fluence values for nanosecond and femtosecond pulse durations. To derive the transmission in open aperture Z-scan data, a theoretical model incorporating one photon, two photon, and free carrier absorptions and their saturations were considered. Nonlinear absorption coefficients and saturation intensity thresholds were extracted from the fitting of the experimental results for both pulse durations used for the experiments. Saturation intensity threshold values in femtosecond regime are significantly bigger than the values in nanosecond regime while nonlinear absorption coefficients values in nanosecond regime are significantly bigger than the values in femtosecond regime. These behaviors are attributed to localized defect states in the energy gap due to the loss of long-range order and defects such as dangling bonds and impurities. With thermal annealing processes at 200 °C and 450 °C nonlinear absorption coefficients and saturation intensity thresholds decrease due to reduction of localized defect states.

1. Introduction

Organic–inorganic nanocomposites have attracted extensive attention in recent years in the open literature. Novel electronic and optical materials based on these composite materials have found applications in technologically demanding areas such as optical switches, optical waveguides and nonlinear optical devices. Carbon supporting transformed the wide band-gap semiconductor oxide into a highly conductive material. The high electrical conductivity of carbon doped TiO_2 was attributed to suboxide formation with substitutional and interstitial carbon, as revealed by XPS and XANES studies. Especially functionalized carbon nanotubes (CNT) have widely been used as a support material due to their special structure, extraordinary mechanical and unique electronic properties [1]. —COOH functionalized CNTs can easily interact with metal atoms of oxide material via oxygen atom (Ti—O—C) on mild conditions and allow the charge transfer [2–5]. Platinum (Pt) is the one of the most active metal, which produce the highest Schottky barrier among metals and allow to electron capture. The captured electrons by Pt are suppress the electron-hole recombination [6]. Pt supported on the CNT doped TiO_2 nanocoating support showed high activity when compared to that of Pt on semiconducting TiO_2 [7].

Hydrothermal carbonization (HTC) is a thermochemical conversion process through which biomass is treated under hot compressed water to prepare carbon support materials (hydrochars). Hydrochar has aromatic structure and large amounts of O-functionalities on their surface. Electron affinity of hydrochar was increased by interaction of these oxygen-containing functional groups with metal oxides [8].

In this paper, we present nonlinear optical absorption behaviors of a different carbon materials supported TiO_2 composites with and without Pt doping. A comparison of green, low cost carbon material derived from hazelnut shell, as a waste biomass, with —COOH functionalized CNT, as a well known support material, was also made. PMMA is one of the most versatile polymeric materials for applications in various technological areas including optics and electro-optics. The unique nonlinear optical behavior of TiO_2/carbon composites was reported in this study. Transparent thin films of TiO_2–PMMA on substrates were synthesized by spin coating.

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The nonlinear absorption in materials exhibits different nonlinear absorption processes such as saturable absorption, reverse saturable absorption, two-photon absorption and multi-photon absorption [9–11]. Nonlinear absorption (NA) can be classified into two types: (i) transmittance increases with increasing optical intensity; this case corresponds to well known saturable absorption (SA); (ii) transmittance reduces with increasing optical intensity; this type includes two-photon absorption (TPA), multi-photon absorption (MPA), and reverse saturable absorption (RSA). TPA process and its saturation have been widely studied in semiconducting crystals [12–14]. NA in amorphous semiconductors can be observed at nonresonant conditions since numerous localized defect states effectively blur the energy gap. SA in thick amorphous semiconductor films was not observed in the literature since especially evaporated thick amorphous semiconductor films have large number of localized defect states [15,16]. The density of the localized defect states in amorphous structure can be changed by thermal annealing. The decrease in the defect density in the structural bonding causes SA or low saturation intensity threshold [17,18]. The nonlinear optical absorption characteristics were investigated using open aperture (OA) Z-scan technique at 532 nm for 4 ns and 800 nm for 200 fs pulse durations. Here we also study the nonlinear absorption phenomenon of the investigated samples at different temperatures. To derive the transmission in the OA Z-scan data, a theoretical model incorporating TPA and its saturation was considered. Nonlinear absorption coefficients and saturation intensity thresholds were extracted from the fitting of the experimental results.

To the best our knowledge, there are lots of studies optical and nonlinear optical properties of TiO_2 nanoparticles in solution and films but there is no study about nonlinear optical properties of TiO_2 nanoparticles with C, CNT and Pt composites. In this paper, we systematically investigated the effect of different TiO_2/carbon composites on nonlinear absorption characteristics.

2. Experimental

TiO_2 nanoparticles were synthesized via solvothermal route at 260 °C for 6 h. Titanium tetra isopropoxide (TTIP) used as a Ti precursor. The procedure was given in our previous study in detail [19]. Composite materials were prepared using with TiO_2 and different carbon materials such as carbon nanotube (multi walled, —COOH functionalized), hazelnut shell based hydrochar. Carbon nanotubes were purchased from Sigma Aldrich and used without further purification. Hazelnut shell based hydrochar was prepared via hydrothermal carbonization (HTC) method at 260 °C for 4 h in an autoclave. Details of the procedure were described in our recent paper [20]. C/TiO_2 composite materials were obtained by mixing specified amount of carbon precursor (hydrochar and CNT) and TiO_2 nanoparticles (1:4) in water-ethanol solution (%50 v/v) at 1500 rpm for 24 h. Obtained materials were separated from the solution via vacuum filtration and dried in an oven at 95 °C for 12 h. According to changing carbon precursors, prepared composite materials were labelled as CNT/TiO_2 and HC/TiO_2. CNT/TiO_2-Pt composite was synthesized via chemical photodeposition method. The required amount of $H_2PtCl_6{\cdot}6H_2O$ for % 1 metal loading was dissolved in ethanol/water (%50 v/v) solution. Afterwards, TiO_2 particles were added into the solution and the mixture was sonicated for 30 min, to improve dispersion. The photo deposition process was performed under UV irradiation (UV-A, 96 W) for 3 h. At the end of the three hours, specified amount of CNT powder was added to the mixture and stirred 24 h in the absence of UV light. Obtained CNT/TiO_2-Pt powder was separated from the solution via vacuum filtration and dried in an oven at 95 °C for 12 h.

Fabrication of the TiO_2/polymer films was investigated with 1 g/10 ml solution of PMMA in chloroform. This PMMA solution was kept in low power sonic bath for 24 h until completely dissolved. Then PMMA solution which used for coating film was prepared with weight percentage of the investigated samples of 25 wt% in PMMA. The solutions were stirred 12 h until homogenous solution was formed. Solid state films of investigated samples were produced on fused silica substrate rotated with speed of 1500 rpm for 1 min by using conventional spin coating system (SCS-Spin Coat G3P). The thermal annealing processes were performed in vacuum (Brother Furnace, XD-1200NT) at 200 °C and 450 °C temperatures. The structural analysis of the films were carried out by using X ray diffraction (XRD) technique varying the diffraction angle $2\theta = 10–90°$ range using Cu K_α radiation. The XRD spectra revealed that all nanocomposite thin films exhibited amorphous behavior. There is no remarkable change in the amorphous structure after annealing process. Transmission electron microscopy is used for determining the particle size of the TiO_2 (FEI Technai G2 S-Twin). The absorption spectra of investigated thin films were measured by using UV–Vis absorption spectrophotometer (Shimadzu UV-1800). The nonlinear absorption properties of investigated TiO_2 PMMA films were measured by using OA Z-scan technique with nanosecond and femtosecond pulse duration as described in literature [21]. Nanosecond laser source is Q switched Nd:YAG laser with 4 ns pulse duration, 532 nm wavelength and 10 Hz repetition rate (Quantel Birillant). Femtosecond laser system is Ti:sapphire laser amplifier– optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS) with 200 fs pulse duration, 800 nm wavelength and 1 kHz repetition rate.

3. Results and discussion

Fig. 1 plots the linear absorption spectra of TiO_2, HC/TiO_2, CNT/TiO_2, CNT/TiO_2-Pt composite films. It shows that all four samples are transparent in the visible region. The onset of absorbance for films, as a result of the excitation of electrons from the valence band to the conduction band, is observed at the wavelength of about 300 nm. The band gap energy, E_g, of the samples near the absorption edge can be further determined using the following expression:

$$(a_0, h\upsilon)^2 = A(h\upsilon - E_g) \quad (1)$$

where α_0 is the linear absorption of the samples which is normalized to the thickness, $h\upsilon$ is the incident photon energy and A is a constant. The thickness of the samples as determined by spectroscopic ellipsometry is 2 μm for all samples. Fig. 2 shows the intercepts of tangents to the $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) plots, estimating a band gap energy of 4.27, 4.44, 4.40 and 4.39 for TiO_2,

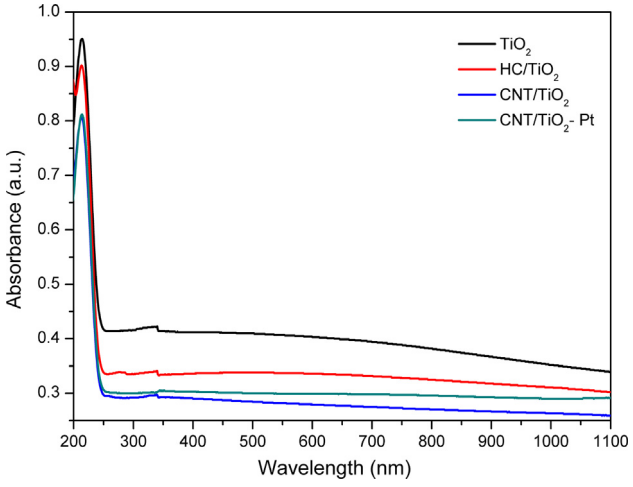

Fig. 1. Linear absorption spectra of thin films in PMMA.