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Synthesis of TiO_2-ZnO-ZrO_2 Nanocomposites for Nonlinear Optics Applications

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ABSTRACT: A sol-gel technique under ultrasonic irradiation was applied to synthesize ZrO_2/TiO_2/ZnO nanocomposites. X-ray diffraction analysis confirmed the successful synthesis of nanocomposites. The strain and crystalline size values of ZrO_2/TiO_2/ZnO nanocomposites are estimated to be 9.98×10^{-4} and 17.66 nm, respectively. The linear absorption coefficient of ZrO_2/TiO_2/ZnO nanocomposites was measured 2.48 cm^{-1} by placing the sample at the focal point of the laser beam, varying the incident power, and recording the output power. The measurements of nonlinear optical absorption of ZrO_2/TiO_2/ZnO nanocomposites have been performed using a continuous-wave Nd: YAG laser operating at 532 nm by the open aperture Z-scan technique. The nonlinear absorption coefficient, β of ZrO_2/TiO_2/ZnO nanocomposites was obtained of the order of 10^{-5} cm/W. The results suggest that ZrO_2/TiO_2/ZnO nanocomposites with a strong nonlinear optical absorption response can be a very promising nonlinear medium that can open a new avenue to the semiconductor-based nonlinear optics.

Keywords: *Nonlinear optics, Sol-gel method, ZrO_2/TiO_2/ZnO Nanocomposites, Z-scan technique.*

INTRODUCTION

Demand for materials with a strong nonlinear optical response is growing in the laser technology and optoelectronics industry. The use of photons instead of electrons is the basis of the nonlinear optical materials used in lasers, data storage, optical communication networks, and optical signal processing applications. Nonlinear optics is a rapidly developing field of modern physics, investigating the behavior of light in nonlinear media and the interaction of a high-intensity coherent source of light with materials. The phenomena such as self-focusing, high-harmonic generation, self-phase modulation, four-wave mixing, formation and propagation of soliton, and various types of simulated light scattering are the nonlinear optical effects [1]. The study of nonlinear optical parameters such as the nonlinear absorption coefficient, nonlinear refractive index, and third-order nonlinear susceptibility evaluations makes it possible to investigate the nonlinear optical behavior of materials when they encounter a high-intensity coherent source of light. It is always an interesting subject of research to synthesize the materials with a strong nonlinear optical response, as it plays an important role in the development of high-performance nonlinear optical

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devices. Semiconductors are the most important materials with widespread applications in optoelectronics technology. Among them, TiO_2, ZnO, and ZrO_2 are the wide bandgap functional semiconductor materials that have a good ability to apply in the fast optical communications, all-optical switching, and optical limiting fields. So far, studies on the nonlinear optical properties of ZnO, TiO_2, ZrO_2 have exclusively focused on undoped and doped with the other materials as composites [2-7]. So not only has there been no research on ternary compounds, there are no reports on binary compounds either.

In this report, we explore the synthesis of a nanocomposite based on transition metal oxides in the system of $ZrO_2/TiO_2/ZnO$ nanocomposites by using the sol-gel technique under ultrasonic irradiation. The structural properties of $ZrO_2/TiO_2/ZnO$ nanocomposites were investigated using XRD analysis. The Z-scan technique was applied to investigate the nonlinear optical properties of $ZrO_2/TiO_2/ZnO$ nanocomposites at a pump wavelength of 532 nm. Open aperture Z-scan measurements were performed and a mechanism for the origin of the nonlinearity of $ZrO_2/TiO_2/ZnO$ nanocomposites synthesized by the sol-gel method was discussed. To the best of our knowledge, the current work is the first report of the nonlinear optical properties of $ZrO_2/TiO_2/ZnO$ nanocomposites.

EXPERIMENTAL PROCEDURE

Materials

Zirconium (IV) chloride anhydrous (99.0%), ammonium solution (28%), Isopropanol (99.5%), acetic acid (99%), ethanol (95%), titanium tetraisopropoxide (97%) and zinc acetate dihydrate (98%) were purchased from Merck Company.

Synthesis of $ZrO_2/TiO_2/ZnO$ nanocomposites

In the first step, 0.01 moles of $ZrCl_4$ was dissolved in 50 mL of Isopropanol to get a precursor solution. A solution of NH_4OH was then dropped into the precursor solution under stirring until the pH of the solution reaches 9. In the second step, 0.01 moles of titanium tetraisopropoxide was dissolved in 20 mL of Isopropanol. In another container, the distilled water, acetic acid, and ethanol were added together in the same ratio. Then, the contents of the second container were added dropwise to the first container under stirring. Stirring continued for one hour to obtain a pale yellow transparent titanium sol.

In the third step, 0.01 moles of $Zn(CH_3COO)_2.2H_2O$ was dissolved in 50 mL of distilled water. Then, one molar aqueous solution of NH_3 was dropped into the zinc acetate solution until a white precipitate of $Zn(OH)_2$ has appeared. Further addition of ammonium solution dissolved the precipitate and the white zinc sol was formed. The three prepared gels were directly mixed to get the $ZrO_2/TiO_2/ZnO$ composite gel. As aging time, the mixture of reaction continuously stirred for 72 hours. The solution was sonicated by an Ultrasound Horn for 30 min to achieve a $ZrO_2/TiO_2/ZnO$ homogenous gel. After filtering, the product was calcinated in the furnace at 500 °C for 4 h. The white powder of $ZrO_2/TiO_2/ZnO$ nanocomposites was prepared.

Materials characterization

The X-ray powder diffraction patterns were recorded on a Philips X'pert MPD Model X-ray diffractometer (XRD) with CuKα radiation (λ=1.5460 Å) under 0.02 o/s at 40 kV of voltage and 40 mA of current in the scan range of 2θ from 20 up to 100 degrees. The linear absorption coefficient of $ZrO_2/TiO_2/ZnO$ nanocomposites was calculated by measuring the power of a CW Nd: YAG laser at 532 nm with and without the cell containing the sample at low power. To calculate the nonlinear optical parameters of $ZrO_2/TiO_2/ZnO$ nanocomposites, the Z-scan technique was applied. The schematic experimental setup arranged for the Z-scan technique is presented in Fig. 1. In this Z-scan experiment, a laser beam irradiated from a second harmonic continuous-wave Nd: YAG laser operating at 532 nm was focused using a lens with a 10-mm focal length producing a beam waist radius of about 25 μm.

The samples were moved along the path of the laser beam between +z and -z positions and the transmitted intensity through the samples was collected in two open and closed-aperture Z-scan regimes.

In the closed-aperture Z-scan setup, an iris diaphragm was placed in the far-field and front of the detector to prevent some of the light to reach the detector leads to an S= 0.28. In the open-aperture regime of

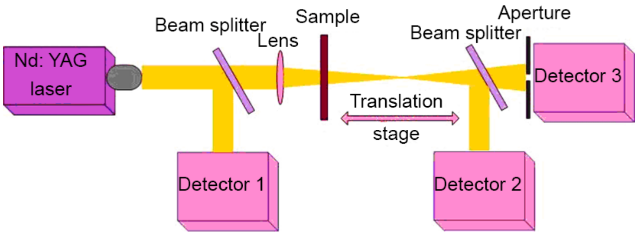

Fig. 1. The experimental setup for the measurement of the nonlinear optical parameters in $ZrO_2/TiO_2/ZnO$ nanocomposites synthesized by the sol-gel method.

Z-scan measurements, the iris diaphragm is removed and the total radiation allowed to pass through the cell containing the $ZrO_2/TiO_2/ZnO$ nanocomposites and recorded by the detector (S= 1). The current Z-scan setup was previously applied to investigate the third-order optical nonlinearity of ZnO/HfO_2 core/shell nanorod arrays [6] and Al-doped ZnO thin films at different Al/ZnO ratios [7].

RESULTS AND DISCUSSION

Structural studies

XRD patterns of $ZrO_2/TiO_2/ZnO$ nanocomposite are shown in Fig. 2. The XRD pattern shows a mixture of both monoclinic (JCPDS card No. 37-1484) and tetragonal (JCPDS card No. 79-1771) phases of ZrO_2, wurtzite-type hexagonal crystalline structure (JCPDS 36-1451) of ZnO, and a mixture of both anatase and rutile phases of TiO_2. To estimate the crystallite size and the strain of $ZrO_2/TiO_2/ZnO$ nanocomposites, the Williamson-Hall method was applied using the $\beta\cos\theta=0.9\lambda/D+4\varepsilon\sin\theta$ equation, where D is the average crystalline size in nm, λ is the wavelength of X-ray source (0.15406 nm), β (in radian) is full width at half maximum of the peaks and ε is the strain of lattice [8]. The strain and average crystallite size values can be estimated by plotting the $\beta\cos\theta$ against $4\sin\theta$ to get a straight line with slope ε and intercept $0.9\lambda/D$. The strain and crystalline size values of $ZrO_2/TiO_2/ZnO$ nanocomposites are estimated to be 9.98×10^{-4} and 17.66 nm, respectively.

Linear optical investigations

To calculate the linear absorption coefficient of $ZrO_2/TiO_2/ZnO$ nanocomposites, the final powder was dispersed in water in a ratio of 1:3 and then sonicated for 10 min to attain a homogenous suspension solution. The resultant solution was poured into a 1-mm quartz cell and placed in the sample holder of the Z-scan configuration. In this arrangement, the Nd: YAG laser that used in the Z-scan measurements, was applied at low incident power and the position of the sample was fixed near the focus of the lens. The laser power measured before and after passing through the sample.

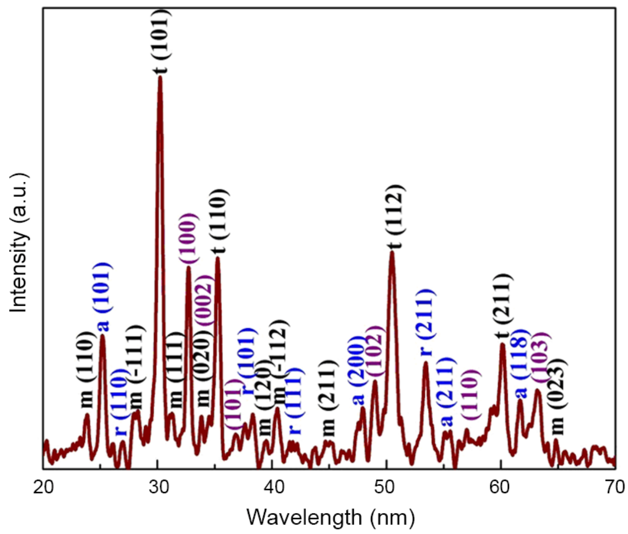

Fig. 2. XRD pattern of $ZrO_2/TiO_2/ZnO$ nanocomposites. The diffraction peaks marked in black indicate monoclinic (m) and tetragonal (t) phases of ZrO_2. The diffraction peaks marked in purple and blue represent the wurtzite-type hexagonal crystalline structure of ZnO and anatase (a) and rutile (r) phases of TiO_2, respectively.

The input power of the laser beam was changed and

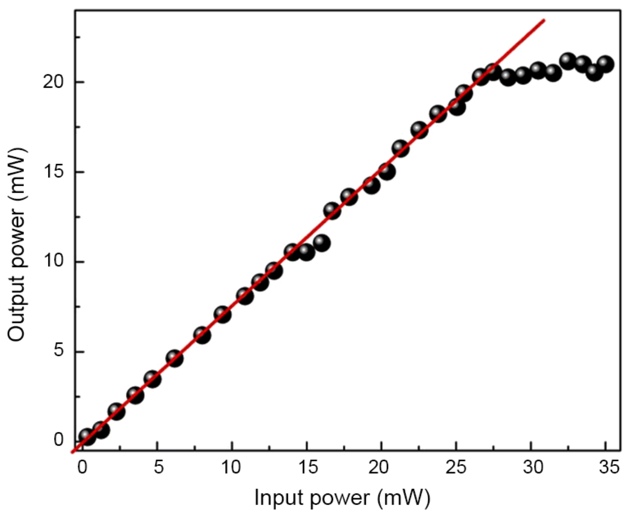

Fig. 3. Output power versus input power plot of $ZrO_2/TiO_2/ZnO$ nanocomposites prepared by the sol-gel method.

then divided in half by using a 50 % beam splitter. The input and output power were recorded using two power meters before and after passing through the cell. Fig. 3 shows the output power of the laser beam as a function of incident power for $ZrO_2/TiO_2/ZnO$ nanocomposites in the range of 0–35 mW.

As can be observed from Fig. 3, at incident power above 27 mW, the output power tends to be constant, because its nonlinear absorption coefficient increases as the incident radiation increases and heating due to the laser absorption is the responsible mechanism for changing the absorption coefficient and the optical limiting effect [9]. From Fig. 3, at lower input power there is a linear relationship between the output power and the incident power that obeys the Beer-Lambert law. The linear absorption coefficient of $ZrO_2/TiO_2/ZnO$ nanocomposites can be calculated from the $\alpha = (-1/L)\ \mathrm{Ln}\ (P_{out}/P_{in})$ equation which L is the thickness of the cell containing the sample. By using the ratio $P_{out}/P_{in} = 0.76$ and L= 1 mm, and the linear absorption, α, was calculated as 2.48 cm^{-1}. The linear absorption coefficient will be used in the calculation of the nonlinear absorption coefficient in the next section.

Nonlinear absorption considerations

The process used to prepare the sample for linear absorption measurements was repeated here. A Z-scan experimental setup shown in Fig. 1 was used to evaluate the nonlinear absorption coefficient of $ZrO_2/TiO_2/ZnO$ nanocomposites. One test found that the response of deionized water was negligible that way a quartz cell containing the deionized water without $ZrO_2/TiO_2/ZnO$ nanocomposites moved along with the laser beam and no significant signal was received via detectors. The result of this test shows that the nonlinear optical responses observed in the current Z-scan experiments are due to the presence of $ZrO_2/TiO_2/ZnO$ nanocomposites dispersed in deionized water.

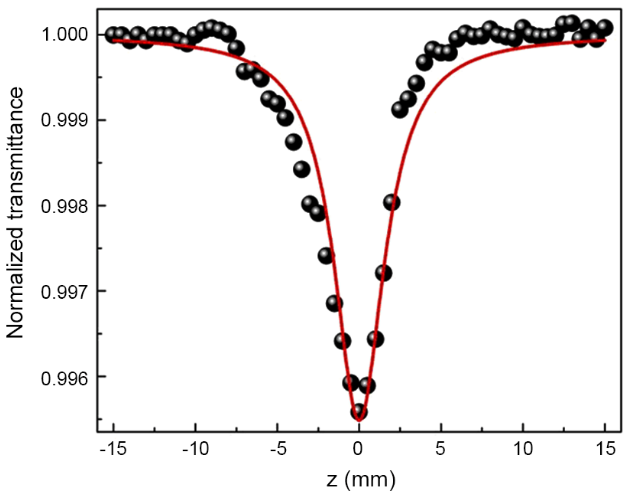

Fig. 4. The normalized transmittance and theoretical simulation curves (solid lines) as a function of sample position in the open aperture Z-scan configuration for $ZrO_2/TiO_2/ZnO$ nanocomposites.

In the open aperture Z-scan, the aperture was removed in Fig. 1 and the transmitted beam reached the detector without any limitation. Fig. 4 shows the resultant data of the open aperture Z-scan experiment for $ZrO_2/TiO_2/ZnO$ nanocomposites. The measurement of the normalized transmittance versus sample position, in the open aperture regime, allows one to determine the magnitude and the sign of the nonlinear absorption coefficient, β.

From Fig. 4, it is seen that the open aperture transmittance has a minimum means that β is negative for $ZrO_2/TiO_2/ZnO$ nanocomposites. The presence of a minimum in the open aperture transmittance data indicates the reverse saturable absorption kind of action in the $ZrO_2/TiO_2/ZnO$ nanocomposites at 532 nm. In the reverse saturable absorption action, the light absorption of the matter is increased compared to the linear regime so that reverse saturable absorbers can be used as optical limiters to protect the sensitive optical components and human eyes from the laser damages [10]. The nonlinear absorption coefficient β can be calculated by fitting the open aperture Z-scan trace with the following equation [11]:

$$T_{open} = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \quad (1)$$

where T_{open} is the normalized transmittance for the open-aperture Z-scan experiment. Besides, q_0 is a factor defined as $q_0=\beta I L_{eff}/(1+z^2/z_0^2)$ that Leff is the effective length of the sample that is estimated by using $L_{eff}=(1-e^{-\alpha l})/\alpha$ relation which l is the thickness of the cell containing the sample and α is the linear absorption coefficient of the sample that was calculated according to the Beer-Lambert formula in the previous section. Furthermore, I is the on-axis irradiant at the focal point illustrated as $I=2P_{laser}/\pi\omega_0^2$ and the diffraction length of the beam (Rayleigh length) in above equation represented as $z_0 = \pi\omega_0^2/\lambda$, where P_{laser} is the incident power of the laser, ω_0 is the radius of the beam at the focal point and λ is the wavelength of the input beam. The symbol 'm' in this theoretical transmittance equation accounts for the orders of the multi-photon absorption; m = 1 holds for two-photon absorption and m = 2 for three-photon absorption etc.

A numerical fit to Eq. (1) gives the estimated values of β as equal to 2.69×10^{-5} cm/W. The results of data fitting showed the highest compliance between experimental data and the fitted curves for m=1 in the theoretical transmittance equation which corresponds well with the two-photon absorption process. It is pertinent to note that the two-photon absorption mechanism is involved in the absorption of a pair of photons by a material that can be employed to investigate the intrinsic properties of a material. Furthermore, the Rayleigh diffraction length is obtained as a fitting parameter to be 3.5 mm, where it is close to the Rayleigh diffraction length at the focal plane that was calculated from the setup properties. The matching between the experimental and theoretical values of the Rayleigh diffraction length is another sign of the confirmation of the fitting process. A large value of the nonlinear absorption coefficient calculated by using the Z-scan setup shows that $ZrO_2/TiO_2/ZnO$ nanocomposites are suitable materials for nonlinear optics applications.

CONCLUSIONS

We have demonstrated the structural and optical characterizations of $ZrO_2/TiO_2/ZnO$ nanocomposites synthesized by the sol-gel method along with the ultrasonic irradiation process. The results of XRD analysis confirmed the formation of monoclinic and tetragonal phases of ZrO_2, the wurtzite-type hexagonal crystalline structure of ZnO, and anatase and rutile phases of TiO_2, respectively. The nonlinear optical absorption measurements of the under investigation sample were performed using a continuous-wave Nd: YAG laser at 532 nm by the Z-scan technique. It was demonstrated that the $ZrO_2/TiO_2/ZnO$ nanocomposites have a good nonlinearity that can be related to the two-photon absorption. The nonlinear optical considerations confirmed that $ZrO_2/TiO_2/ZnO$ nanocomposites are good candidates for application in nonlinear optical devices.

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