3-19-2012

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Parida, Manas R.; Vijayan, C.; Rout, Chandra Sekhar; Sandeep, C.S. Suchand; and Philip, Reji, "Enhanced optical nonlinearity in beta-AgVO3 nanobelts on decoration with Ag nanoparticles" (2012). *Birck and NCN Publications.* Paper 1237.
http://dx.doi.org/10.1063/1.3696301

AIP | Applied Physics Letters

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Citation: Appl. Phys. Lett. **100**, 121119 (2012); doi: 10.1063/1.3696301
View online: http://dx.doi.org/10.1063/1.3696301
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v100/i12
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Enhanced optical nonlinearity in β-$AgVO_3$ nanobelts on decoration with Ag nanoparticles

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(Received 6 May 2011; accepted 8 February 2012; published online 23 March 2012)

This paper reports on the optical nonlinearity of β-$AgVO_3$ nanobelts and the modification in the physical mechanisms of nonlinear response on decorating with silver nanoparticles. The nanobelts are synthesized by a hydrothermal technique and characterized using SEM, TEM, and XRD etc. The nanobelts are found to exhibit large nonlinear optical absorption as revealed by open Z-scan measurements using 5 ns laser pulses at 532 nm. Nonlinearity appears to be arising from a combination of mechanisms of two photon absorption and saturable absorption (SA). Decoration with Ag nanoparticles is found to enhance the saturable absorption and alter the coefficient of nonlinear absorption of the nanobelts. Efficient optical limiting is demonstrated in both the nanobelt systems. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3696301]

Silver vanadium oxides (SVOs) are among the most complicated metal oxides, with a number of phases present even in the case of a single atomic composition. SVOs have been identified to be candidate materials for applications in advanced biomedical devices in view of their ionic properties and electrochemical parameters.[1] A number of SVOs with different structures have attracted recent attention in view of their interesting electronic properties.[2–5] Synthesis of materials with well-controlled size, morphology, and chemical composition can offer great opportunities for exploring their chemical and physical properties and for the fabrication of nanodevices.[2,3] Several techniques for the preparation of SVOs nanostructures have been developed recently. Song *et al.*[3] have reported a solution approach using pyridine for the high-yield synthesis of $AgVO_3$ nanoribbon. Shen and Chen[4] have reported synthesis of $Ag_2V_4O_{11}$ nanorings and microloops formed by the self-coiling of $Ag_2V_4O_{11}$ nanobelts under a hydrothermal process. $Ag_2V_4O_{11}$ nanowires, β-$AgVO_3$ microrods, and β-$AgVO_3$ nanowires have been fabricated via a simple and facile low-temperature hydrothermal approach, and its electrochemical and field-emission properties have been studied.[5,6] In this work, we report on the synthesis, characterization, linear, and nonlinear optical properties of β-$AgVO_3$ nanobelts, as well as Ag-decorated β-$AgVO_3$ nanobelts. Here, we report on the observation of strong nonlinear optical response in these systems. The nonlinearity is shown to arise from a combination of saturable absorption (SA) and two photon absorption (TPA) processes with an enhancement due to silver nanoparticles decoration.

In a typical synthesis of $AgVO_3$ nanobelts, 0.5 g of ammonium metavanadate (Sigma-Aldrich), 40 M of polyethylene glycol-2000, and 1 g of silver nitrate are taken in 30 ml of deionized water and refluxed at 100 °C for 3 h allowing the reactants to dissolve completely. Nitric acid is added dropwise to adjust the *p*H of the solution to ~2. After getting a pure orange colour clear solution, the product is transferred to a 100 ml autoclave and heated at 200 °C for 24 h. The final product obtained after cooling the autoclave to room temperature is washed with deionised water and then with anhydrous alcohol several times and dried at 50 °C for 24 h. For silver incorporation on nanobelts, the concentration of silver nitrate is slowly increased in the above reaction.

The XRD pattern of the as-prepared β-$AgVO_3$ can be indexed to the phase of β-$AgVO_3$ monoclinic structure [JCPDS: 29-11541, lattice parameters: a = 17.85 Å, b = 3.58 Å, c = 8.03 Å] as shown in Fig. 1(a). The (501) peak is the strongest one, indicating the possible preferential orientation of the β-$AgVO_3$ nanobelts. The XRD pattern of Ag-decorated β-$AgVO_3$ nanobelts is shown in Figure 1(b), which shows peaks at angle 38° and 77°, corresponding to crystalline Ag in the cubic structure. All the other peaks match well with those of undecorated β-$AgVO_3$ nanobelts shown in Fig. 1(b).

Fig. 2(a) shows the field emission scanning electron microscope (FESEM) image of the β-$AgVO_3$ nanobelts. The presence of silver, vanadium, and oxygen are confirmed from the energy dispersive x-ray spectroscopy (EDS) shown in Fig. 2(b). The weight percentage of V is 60%, which is much larger than that of Ag and O in the material. Figure 2(c) shows HRTEM image of the nanobelts, and the crystalline structure of nanobelt can be seen clearly in Figure 2(d), image at a higher magnification. The diameter of the nanobelts is in the range of 30–150 nm, with length upto several microns. The inset of Fig. 2(d) is the selected area electron diffraction (SAED) pattern of a nanobelt where the crystal planes are observed clearly.

Fig. 3(a) shows a FESEM image of the nanobelts decorated with Ag nanoparticles. The presence of Ag, V, and O are conformed from EDS shown in Fig. 3(b). The weight percentage of Ag is 58%, which is larger than that of V and O in the material, due to the presence of Ag nanoparticles of surface of nanobelts. Figures 3(c) and 3(d) show HRTEM images from which Ag nanoparticles can be clearly seen to be attached to the β-$AgVO_3$ nanobelts. The composition of

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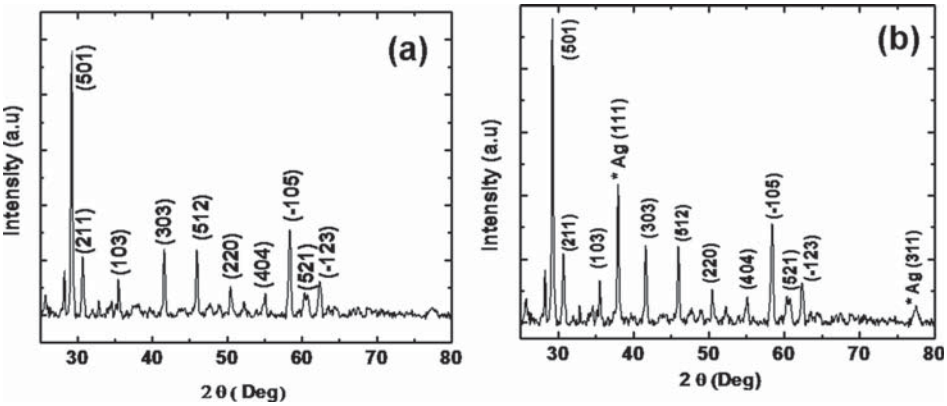

FIG. 1. XRD pattern of (a) β-$AgVO_3$ nanobelts and (b) Ag-decorated on β-$AgVO_3$ nanobelts (* marks show the presence of Ag nanoparticles).

the nanobelts is analysed using EDS pattern, and the spectrum obtained from an individual nanobelt shows the presence of Ag, V, and O with no other impurities. The adjacent lattice planes can be seen in SAED pattern, shown as an inset in Figure 3(d).

We investigate the absorptive nonlinearity by performing open aperture Z-scan measurements at 532 nm using laser pulses of 5 ns pulse duration. For the Z-scan experiments, all the samples are dispersed in ethanol and kept in a quartz cuvette. The cuvette of path length 1 mm is mounted on a translation stage, using which the sample is moved along the beam direction of beam which is intensity-modulated using a lens. All the measurements are carried out at room temperature. In this experiment, nanosecond pulses of two different energies 15 μJ and 30 μJ are used. The pulses of Gaussian cross section are tightly focused on the sample, and transmittance is measured using a detector placed after an aperture in the far-field. Laser pulses of width 5 ns are used at a low repetition rate of 10 Hz for all the experiments to minimise thermal lens effects.

Results of the open aperture Z-scan experiment are shown in Fig. 4. The shapes of the traces are indicative of a reasonably strong nonlinear absorption. The symbols denote experimental data points, and the solid line represents a theoretical fit based on the model discussed below. The open Z-scan curves are normalized with respect to the linear absorption of the sample and, hence, the occurrence of TPA is shown up as a dip in the open Z-scan trace, whereas the occurrence of SA shows up as a peak. The present samples have TPA as the predominant mechanism with the simultaneous occurrence of SA to a smaller extent and, hence, the observed open Z-scan trace exhibits a "wing" structure, which can be readily appreciated in the case of the decorated sample (Fig. 4(b)) while it is not so obvious in the case of bare $AgVO_3$ (Fig. 4(a)).

The data are analysed on the basis of the Sheik Bahae model incorporating the feasible mechanisms for nonlinear absorption. Assuming a Gaussian profile for the laser pulses, the normalized transmittance can be written as[7]

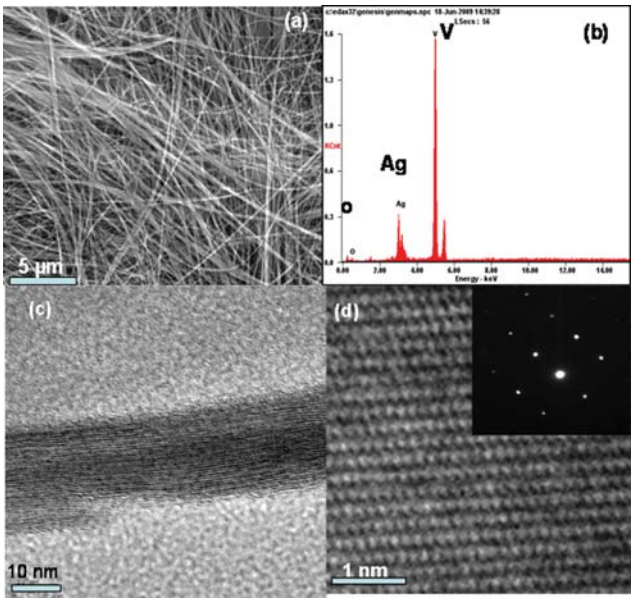

FIG. 2. (Color online) (a) A representative FESEM image of β-$AgVO_3$ nanobelts. (b) EDAX pattern of an individual nanobelt. (c) TEM image of β-$AgVO_3$. (d) HRTEM image of β-$AgVO_3$ with SEAD of β-$AgVO_3$ (inset).

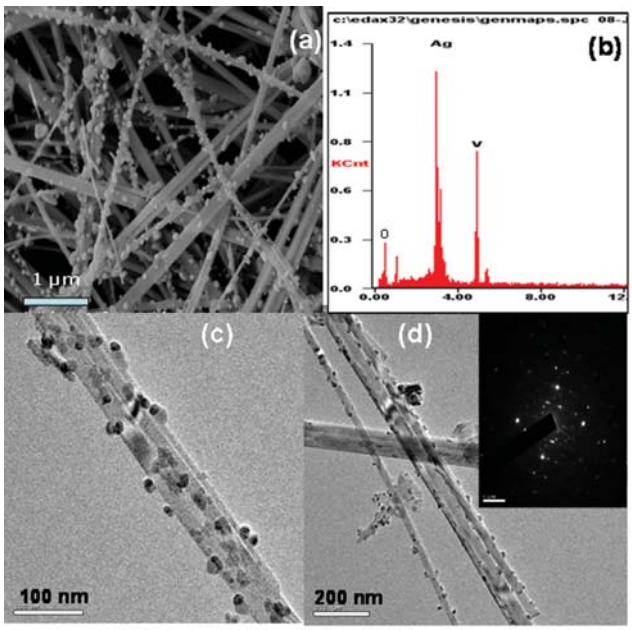

FIG. 3. (Color online) (a) and (b) FESEM image of β-$AgVO_3$ nanobelts decorated with Ag nanoparticles. (c) TEM image of an individual β-$AgVO_3$ nanobelt decorated with Ag nanoparticles. (d) TEM image with SAED pattern (inset) is collected from a Ag nanoparticle.

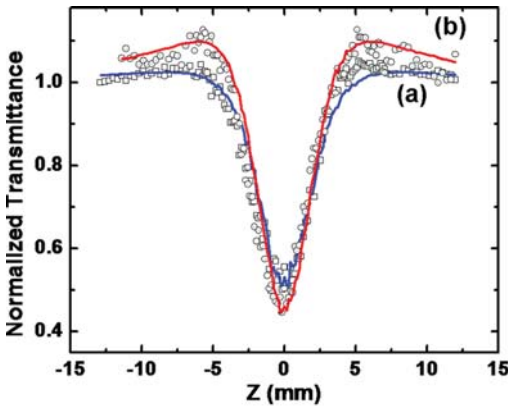

FIG. 4. (Color online) (a) Open Z-scan results of β-$AgVO_3$ nanobelts and (b) open Z-scan results of Ag:$AgVO_3$ nanobelts.

$$T(z) = \frac{1}{\sqrt{\pi}q(z)} \int_{-\infty}^{\infty} \ln\left[1 + q(z)\exp(-\tau^2)\right] d\tau,$$

where $q(z) = \frac{\beta I_0 L_{eff}}{1+(z/z_0)^2}$ with I_o being the peak intensity at the focal point and $L_{eff} = [1 - \exp(-\alpha_o L)]/\alpha_o$ where L is the sample length and $z_o = \pi\omega_o^2/\lambda$, where ω_o is the beam waist and λ is the light wavelength. The nonlinear absorption coefficient is determined from the best theoretical fit obtained for the experimental data. It is found that the theoretical fit using the above equation based on solely two photon absorption does not fit well with the experimental data. Taking into account the fact that SA and limiting kind of absorption are the two probable competing processes, we consider a nonlinear absorption coefficient of the form (Gao *et al.*),[8,9]

$$\alpha(I) = \frac{\alpha_o}{1 + \frac{I}{I_s}} + \beta I.$$

Here I is the laser intensity, I_s is the saturation intensity, and β is the two photon absorption coefficient. Then, the modified normalized transmittance can be written as

$$T(z) = \frac{Q(z)}{\sqrt{\pi}q(z)} \int_{-\infty}^{\infty} \ln[1 + q(z)\exp(-\tau^2)] d\tau,$$

where $Q(z) = \exp(\alpha_o LI/(I + I_s))$ and $q(z) = \alpha_o I_o L_{eff}/1 + (z/z_o)^2$ with I_o being the peak intensity at the focal point. The two photon absorption coefficient β and saturation intensity I_s for β-$AgVO_3$ nanobelts are found to be 9.5×10^{-11} m/W and 1.5×10^{11} W/m^2, respectively. The two photon absorption coefficient β and saturation intensity I_s for Ag supported β-$AgVO_3$ nanobelts are found to be 9.8×10^{-11} m/W and 3.5×10^{12} W/m^2, respectively. However, it must be pointed out that the fitting of the experimental data with the theoretical model involving SA and TPA is not very good in the case of bare $AgVO_3$ (Fig. 4(a)) and the best fit curve given here does not reproduce the small "wing" structure of the data properly. Thus, the value of I_s inferred from this fit may not represent the true extent of SA quantitatively. On the other hand, this feature due to SA is seen unambiguously in the case of the Ag-decorated sample (Fig. 4(b)). Thus, the occurrence of SA in the decorated sample is clearly more prominent than that in the undecorated sample, while a quantitative comparison is difficult. A comparison of the Z-scan traces of the decorated and undecorated samples also indicates an enhancement in the two photon absorption coefficient due to Ag decoration. An enhancement of three photon absorption and self focusing nonlinear refraction has been reported earlier in Mn doped ZnS quantum dots by the using Z-scan technique at 532 nm.[12] Saturation followed by three photon absorption has also been observed earlier in other systems.[13] There is no change observed in nonlinear signal after increasing the input energy from 15 μJ to 30 μJ for both the materials. So the nonlinearity observed in the present case appears to be originating mainly from the two photon absorption along with saturable absorption. The large enhancement in saturation intensity observed in the case of Ag nanoparticles decorated β-$AgVO_3$ nanobelts could be due to surface plasmon effect. The extra Ag nanoparticles available in this system lead to an increase in saturation intensity because of surface plasmon enhancement of the local electric field.[19] The optical absorption data (provided as supplementary material[21]) indicate that the Ag nanoparticles decorated $AgVO_3$ nanobelts exhibit considerable increase in the optical density at 532 nm, the wavelength at which the Z-scan has done. Some increase in the saturable absorption effects can be expected due to the possible contribution form the additional absorption channel provided by ohmic damping of surface plasmon oscillations. This helps to explain qualitatively the observed "wing" feature (Fig. 4(b)) due to SA in the Z-scan trace of the Ag-decorated samples.

In this Z-scan technique, the laser beam is focused using a lens, and the sample is moved along the beam axis (z axis) from one side of the focus to the other, through the focal point. In this scheme, each z position corresponds to an input fluence of $\frac{4\sqrt{\ln 2}E_{in}}{\pi^{3/2}\omega(z)^2}$, where E_{in} is the input laser pulse energy.[10,11]

Optical limiting is investigated in β-$AgVO_3$ nanobelts and Ag-decorated β-$AgVO_3$ nanobelts. The fluence-dependence of transmittance measured at 532 nm is shown in Fig. 5. The limiting threshold is defined as the incident fluence at which the transmittance falls to 50% of the normalized linear transmittance.[20] The optical limiting threshold is 3.7×10^4 J/m^2 in β-$AgVO_3$ nanobelts measured from Fig. 5(a). The optical limiting threshold is 5.9×10^4 J/m^2 in Ag nanoparticles decorated β-$AgVO_3$ nanobelts measured from Fig. 5(b). There are several mechanisms proposed in

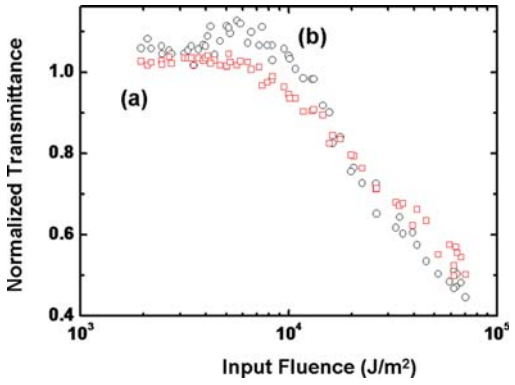

FIG. 5. (Color online) (a) Optical limiting of β-$AgVO_3$ nanobelts and (b) optical limiting of Ag:$AgVO_3$ nanobelts.

the literature to explain the optical limiting effect and the nonlinear absorption such as two-photon absorption, reverse saturable absorption, and nonlinear scattering.[14–18] The optical limiting activity of semiconductor quantum dots was usually described as due to two-photon or three-photon absorption. To confirm the mechanism of the observed optical limiting activities, we have conducted scattering measurements for both the samples. The scattering signals were collected at an angle 45° from the propagation axis of the transmitted laser beam. The contribution from nonlinear scattering became smaller with increasing input laser fluences and became the dominant contribution at high pump fluences. The results suggest that nonlinear scattering has only a limited role in the optical nonlinearity in these materials. It appears that the two photon absorption followed by the saturation absorption is the main reason behind optical limiting in both the samples investigated in the present work.

In summary, SVO nanobelts are shown to exhibit strong nonlinear optical absorption with TPA as the predominant physical mechanism. The effect of decoration with metal nanoparticles is an increase in the saturation intensity and a slight increase in the nonlinear absorption coefficient. This could enhance the performance of the material as a saturable absorber though the performance as efficient optical limiter may not be much different. The origin of nonlinear absorption is a combination of two photon absorption and sturable absorption. The design of different kinds of such nanocomposites helps to combine different mechanisms of nonlinearity of the individual components and achieve probable enhancement which can be of crucial importance to developing candidate materials with optimal parameters of optical response for potential device applications.

We thank the Department of Science and Technology Unit on Nanoscience, IIT Madras for HRTEM. We also thank SAIF, IIT Madras for FESEM, and Defence Research Development Organization (DRDO), Govt. of India, for funding. The authors acknowledge the suggestions made by the reviewer which have helped to improve the quality of the paper considerably.

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[21]See supplementary material at http://dx.doi.org/10.1063/1.3696301 for optical absorption spectra of $AgVO_3$ nanobelts and Ag nanoparticles decorated $AgVO_3$ nanobelts.