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The nonlinear refraction sign turned to reverse by intercalating cresyl violent dye into layered titanate nanosheets

Chunsheng Dou [a], Puhong Wen [b,c,*], Xingang Kong [c], Shunsuke Nakanishi [c], Qi Feng [c]

[a] Department of Physics and Information Technique, Baoji University of Arts and Science, 44 Xibao Road, Baoji, Shanxi 721007, China
[b] Department of Chemistry and Chemical Engineering, Baoji University of Arts and Science, 1 Gaoxin Road, Baoji, Shaanxi 721013, China
[c] Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi, Takamatsu 761-0396, Japan

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ABSTRACT

Solid-state dye-doped materials are an attractive alternative to conventional liquid dye solution. In this study, the spectral characteristics of dye cresyl violet before and after intercalating into layered titanate nanosheets and forming a nanohybrid thin film were investigated by measuring absorption and fluorescence spectra. In addition, their nonlinear optical properties were studied using single beam z-scan technique under irradiation of low power continuous wave (CW) produced by DPSS laser with a wavelength of 532 nm. The nonlinear studying results reveal that the dye cresyl violet in solution has a negative nonlinear refractive index, but it reverses to positive after the dye is intercalated into layered titanate nanosheets with a negative nonlinear refractive index forming CV/HTO nanohybrid thin film. This method can provide a way to turn to reverse nonlinear refraction sign of the materials.

1. Introduction

Some inorganic layered materials have been researched as host compounds for preparing their nanosheets by exfoliation [1]. Exfoliated nanosheets or stacks of a few sheets have potential applications as precursors in the construction of nanocomposites, and in preparations of functional nanostructured materials and thin films with novel properties [2]. The titanate nanosheet with uniform thickness can be obtained by exfoliation of the layered titanate crystal into its elementary host layer in a solution of organic amine [3,4]. Titanate nanosheet is a unique and useful two-dimensional titanium oxide nanomaterial, which is a promising precursor for the preparation of nanostructured materials, such as multilayer thin film by layer by layer stacking of different nanosheets, and nanotubes [5,6].

Refractive nonlinearities associated with self-focusing and self-defocusing in various media are currently being explored with greater interest owing to their increasing application potential in various optical devices. For example, a material with a positive third-order nonlinear refractive index coefficient (n_2), which behaves like a focusing lens, can be used for soliton formation in optical waveguides [7,8], and a material with a negative value of n_2 can be applied as an optical limiter of laser radiation due to the divergence produced by self-defocusing [9,10]. Up to now many studies have been carried out to obtain the materials with nonlinearity refractive index by some methods, such as doped between semiconductors, insulator-doped semiconductor, dye-doped polymers or inorganic matter and so on [11–15]. And the majority focuses on increasing magnitude of n_2 of nonlinear optical materials [16–18]. It is almost found without reported turned to reverse of sign of n_2 of nonlinear optical material, Li et al. report about the changing of index sign from positive to negative in an organic–inorganic hybrid film doped covalently by azobenzene dye in 2008 [19]. Very recently, we find a novel phenomenon that the third-order nonlinear refractive index coefficient sign of cresyl violet (CV) dye and titanate nanosheet film can be changed from negative to positive when the dye is intercalated into titanate nanosheet forming hybrid film under continuous wave (CW) illuminations. This is a well-known self-focusing nonlinear optical phenomenon which can be used in many optical devices. No work has been reported on the study of nonlinear refractive index of cresyl violet dye intercalated into titanate nanosheets.

In the present paper, we describe a nanohybrid thin film prepared by intercalating CV dye molecules into titanate nanosheets and characterization of its optical properties. We investigate the fundamental optical properties by measuring the absorption and fluorescence spectra of the dye before and after intercalated in the nanohybrid film. The nonlinear optical properties of the dye intercalated in the nanohybrid film have been studied under the irradiation of low power continuous wave (CW) produced by DPSS laser with a wavelength of 532 nm using single beam z-scan technique [20]. Such nanohybrid materials of titanate nanosheets with dye molecules, where the dye formed so-called H-aggregates in

* Corresponding author. Department of Advanced Materials Science, Faculty of Engineering, Kagawa University, 2217-20 Hayashi, Takamatsu 761-0396, Japan. Tel.: +81 87 864 2410; fax: +81 87 864 2438.
E-mail address: wenpuhong@gmail.com (P. Wen).

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the interlayer space [21] and acted as sensitizers, can be used as electronic and optical devices. The materials with controlled and defined nanostructures are valuable to fundamental studies of photo processing in dye-sensitized semiconductor systems in order to optimize the material performance [22,23].

2. Sample and experiment

2.1. Preparation of titanate nanosheet

The titanate nanosheets were prepared by the method in reference [24], first a layered titanate of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (KTLO) with lepidocrocite-like layered structure was prepared by hydrothermal method. 5.1 g KOH, 0.6 g of $LiOH \cdot H_2O$, 6.9 g of TiO_2 (anatase) and 25 mL of distilled water were sealed into a Hastelloy-C-lined vessel with internal volume of 45 mL, and then heated at 250 °C for 24 h under stirring conditions. After the hydrothermal treatment, the sample was washed with distilled water, and dried at room temperature to obtain KLTO. KLTO (10 g) was treated with a 0.2 mol L^{-1} HNO_3 solution (1 L) for 1 day under stirring conditions to exchange K^+ and Li^+ in the layered structure with H^+, and then the sample washed with distilled water. After 2 times of the acid treatment, an H^+-form layered titanate $H_{1.07}Ti_{1.73}O_4 \cdot nH_2O$ (HTO) was obtained.

The layered titanate nanosheet colloidal solution was prepared by exfoliating HTO using an exfoliating reagent of tetramethylammonium hydroxide (TMAOH). In the preparation of TMA-HTO nanosheets colloidal solution, HTO (10 g) was treated in a 0.016 mol L^{-1} TMAOH solution (2 L) under stirring conditions at room temperature for 7 days.

2.2. Preparation of CV/HTO nanohybrid and HTO thin films

The dye, cresyl violet (CV) purchased from Exciton Inc. USA was chosen for this study. Fig. 1a shows the structure of CV dye. The CV/HTO nanohybrid materials can be prepared by intercalating reaction between the dye and titanate nanosheets. First the nanosheets colloidal solution was mixed with CV dye solution with a concentration of 5.0×10^{-5} mol L^{-1} in the ratio 1:1 (V/V) at room temperature. After the reaction, the product was separated from the solution by centrifugation, washed with distilled water, and then dispersed in distilled water to obtain CV/HTO nanohybrid colloidal solution. The nanohybrid colloidal solution was dropped on a glass substrate and then was dried to obtain a CV/HTO nanohybrid thin film. The HTO thin film was prepared by dropping the TMA-HTO nanosheets colloidal solution on a glass substrate and then was dried at room temperature. The thickness of thin films was 3.21×10^3 nm for CV/HTO and 1.78×10^3 nm for HTO, respectively, measured using a SURFCOM 480 A surface shape determinator.

2.3. TEM, HRTEM and SAED analysis

Transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM) and selected-area electron diffraction (SAED) observation were performed on a JEOL JEM-3010 at 300 kV, and the sample was supported on a microgrid.

2.4. Spectral measurements

The spectral properties of the samples were studied by recording the absorption and fluoresces spectra using JASCO V-530 UV/vis spectrophotometer and HITACHI F-2500 spectrofluorometer, respectively. Care was taken to record all spectra under identical conditions. Besides, powder X-ray diffraction (XRD) analysis of the samples were also carried out on a SHIMADZU XRD-6100 X-ray diffractometer with Cu Kα ($\lambda = 0.15418$ nm) radiation.

2.5. Nonlinear refractive index measurement

The excitation source used in the present study was a 5 mW CW DPSS (diode pumped solid state) laser with operating wavelength of 532 nm. A lens with a focal length of 6 cm focused the laser beam. The sample was moved along the *z*-axis through the focal point. The spot size of focused beam was measured to be 55 μm and the diffraction length, Z_0, was 17.9 mm, which corresponded to the intensity 1.05×10^6 W/m^2 at the center. The transmitted radiation is collected through a far field aperture with a phototransistor. This experimental setup with a closed aperture shown in Fig. 2 allowed us to determine the sign and magnitude of the nonlinear refractive index, n_2. Since the thickness of sample was much less than the diffraction length of the focused beam, the analysis of the data can be treated approximating according to case of a thin sample [20].

3. Results and discussion

3.1. The CV/HTO nanohybrid thin film formed by intercalating CV dye molecules into titanate nanosheets

KTLO with a lepidocrocite-like layered structure (orthorhombic, space group: Cmcm, $a = 0.376$, $b = 0.783$, $c = 0.297$ nm) can be transformed to layered HTO by acid treatment [4]. The HTO can be exfoliated into titanate nanosheets by organic amine, such as TMAOH solution. Fig. 3 shows TEM (a) and HRTEM (b) images of the titanate

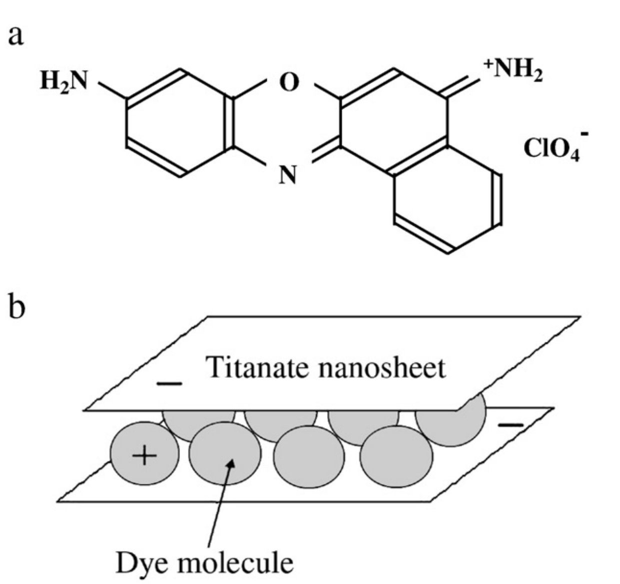

Fig. 1. (a) Molecular structure of cresyl violet and (b) schematic illustration of the structure of dye intercalated in titanate nanosheets.

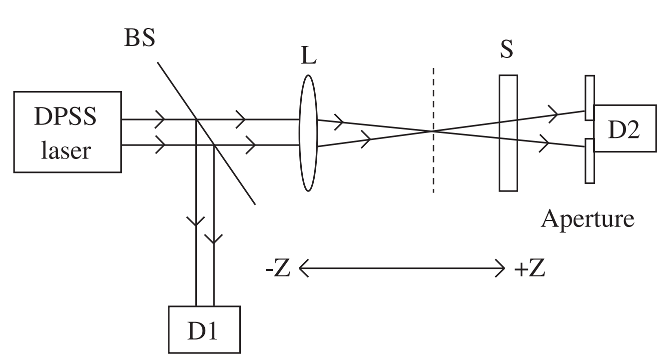

Fig. 2. The closed of z-scan setup. D1, D2, detectors; BS, beam splitter; L, convex lens; S, sample.