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Formation of aggregates in nanohybrid material of dye molecules–titanate nanosheets

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ABSTRACT

Nanohybrid solution and thin film of Rhodamine 6G (R6G) or pseudo-isocyanine (PIC) with the titanate nanosheets (HTO) of $H_{1.07}Ti_{1.73}O_4{\cdot}nH_2O$ with a lepidocrocite-like layered structure were fabricated by using a soft chemical process. The optical properties of the nanohybrids were investigated by absorption and fluorescence spectroscopies. An H-aggregate of the R6G molecules was formed in the R6G–HTO nanohybrid system, while a J-aggregate of the PIC molecules was formed in the nanohybrid PIC–HTO system. Fluorescence quenching behavior was observed in both of the R6G–HTO and PIC–HTO nanohybrid systems.

1. Introduction

Titanium oxide is an important metal oxide semiconductor material that has been widely used for several applications such as white pigments, opto-electronics materials and photocatalysts [1]. Especially, much attention has been paid to nanostructured titanium oxides adsorbed dye molecules for visible light sensitive photocatalysts and dye-sensitized solar cells [2]. In the nanostructured titanium oxides, such as nanoparticles, nanotubes and nanosheets, high performance of the device functions is expected since adsorptive capability of the dye molecule can be improved. Therefore, the investigations of the optical and electronic properties of nanostructured titanium oxides adsorbed dye molecules are very important.

The exfoliation reaction of layered compounds is a unique and useful technique for the preparation of two-dimensional nanomaterials. In this reaction, a bulk crystal of the layered compounds can be exfoliated into its elementary host layers, meaning nanosheets with uniform thickness of about 1 nm in a solution [3]. Such nanosheets are promising precursors for the preparation of nanostructured materials, such as multilayer thin film by layer-by-layer stacking of different nanosheets [4], nanotubes [5] and particles [6] by modifying its morphology and structure. The titanium oxide nanosheets can be obtained also by using the exfoliation reaction. It has reported that a layered titanate $H_{1.07}Ti_{1.73}O_4{\cdot}nH_2O$ (HTO) with lepidocrocite-like structure can be exfoliated into its elementary nanosheets in a organic amine solution [7–9].

While, the optical properties of dye-molecule-intercalated layered compounds such as clay have been studied extensively for the application to novel solid state laser material [10–13]. In the interlayer space of the layered compound, the uniform aggregates of the dye molecules are formed easily because the self-assembling of the dye molecules occurs easily in the interlayer space, which causes the orientation arrangement of the molecules. The configuration of molecular aggregation drastically changes the absorption and florescence properties of the dye molecules, which is depend on the relative orientation of the transition moment vector of the molecule in the aggregate [12]. When the transition dipole moment direction of molecules is coplanar and in-line, which is called J-aggregate, the absorption band is placed at lower energy side with respect to the monomer absorption band. On the other hand, when the transition dipole moment direction of molecules is aligned and in parallel plane, which is called H-aggregate, the absorption band is shifted to higher energy side with respect to the monomer absorption band. In the H-aggregate, the fluorescence is quenching.

In the present study, we describe nanohybrid solution and thin film fabricated by assembling the layered titanate nanosheets and dye molecules, and characterization of their optical

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properties. Such nanohybrid materials of dye molecules and titanate nanosheets have potential applications to novel functional optical devices such as dye sensitized photo-sensors, photocatalyst and photovoltaic solar cell. In this paper, we investigated the fundamental optical properties of absorption and fluorescence for two kinds of dyes, Rhodamine 6G (R6G) and pseudo-isocyanine (PIC) in the nanohybrid materials.

2. Experimental procedure

2.1. Sample preparation

In the synthesis process of the layered titanate nanosheets [6], first a layered titanate of $K_{0.8}Ti_{1.73}Li_{0.27}O_4$ (KTLO) with a lepidocrocite-like layered structure was prepared by hydrothermal method. KOH (5.1 g), $LiOH{\cdot}H_2O$ (0.6 g), TiO_2 (6.9 g) and distilled water (25 mL) 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 M 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 was 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 agent of tetramethylammonium hydroxide (TMAOH). In the preparation of TMA–HTO nanosheet colloidal solution, HTO (10 g) was treated in a 0.016 M TMAOH solution (2 L) under stirring conditions at room temperature for 7 days.

The nanohybrid material of dye–titanate nanosheet was prepared by reaction of the nanosheet colloidal solution with an aqueous solution of dye at room temperature. First the nanosheet colloidal solution was mixed with the dye solution at room temperature. In this reaction, the negatively charged titanate nanosheet attracted the positively charged dye molecules on its surface, and formed the nanohybrid of dye–titanate nanosheet in the solution. After the reaction, the product was separated from the solution by centrifuge, washed with distilled water, and then dispersed in distilled water to obtain a dye–titanate nanosheet nanohybrid colloidal solution. The nanohybrid colloidal solution was casted on a glass substrate, and then dried at room temperature to obtain a dye–HTO nanohybrid thin film. In the drying process, the dye–adsorbed HTO nanosheets restack together, and formed a layered structure with the dye molecules in the interlayer space on the surface of the substrate. Fig. 1(a) shows the schematic illustration of the structure of the nanohybrid thin film of dye molecules and HTO nanosheets (dye–HTO).

In this study, we utilized Rhodamine 6G (R6G) and pseudo-isocyanine (PIC) as the dyes for the nanohybrids with HTO nanosheets. Fig. 1(b) and (c) shows the structures of R6G and PIC molecules, respectively. Here, the size of each molecule was calculated by a force filed molecular mechanics (MM2) calculation. The molar ratios of R6G and PIC to TiO in the nanohybrid are 0.027:1 and 0.022:1, respectively, measured by Thermo-gravimetric Differential Thermal Analysis (Shimadzu, DTG-60H).

2.2. Structural analysis

Powder X-ray diffraction (XRD) analysis of the samples was carried out on a SHIMADZU XRD-6100 X-ray diffractometer with Cu Kα (λ = 0.15418 nm) radiation. Transmission electron microscope (TEM) observation was performed by a JEOL JEM-3010 at 300 kV, and the sample was supported on a micro grid.

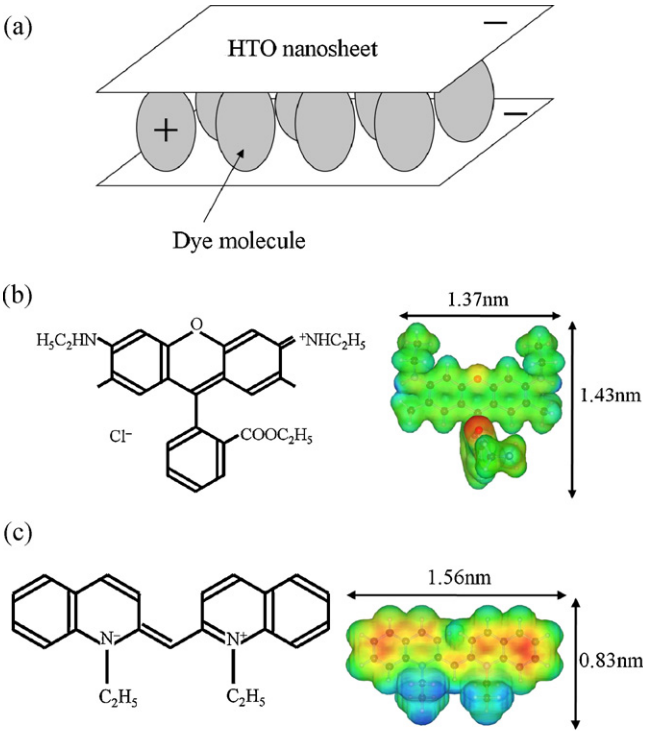

Fig. 1. Schematic illustration of the structure of dye–HTO nanohybrid (a), molecular structures of R6G (b) and PIC (c).

2.3. Optical properties

Absorption and fluorescence spectra of the aqueous solution of mono-dispersed pure R6G and PIC dye molecules and the colloidal solutions of the R6G–HTO and PIC–HTO nanohybrids were measured at room temperature by a spectrophotometer (JASCO, V-530) and a fluorescence spectrophotometer (HITACHI, F-2500), respectively.

Polarization dependence of absorption properties of the dye–HTO nanohybrid thin film was measured using experimental setup as shown in Fig. 2. White light from a halogen lamp was polarized by passing through a polarizer. The polarization angle was 0° (x-polarized) or 90° (y-polarized). The incident angle α was changed from 0° to +45° by tilting the sample. The transmitted light was incident on a spectrometer (JASCO, CT-250) and then detected by a CCD camera (Prinston Instruments, NTE 2/CCD, 1024 × 256 pixel). By the peak analysis of the obtained absorption spectra, absorbance dichromatic ratio between in the x-polarized and y-polarized A_y/A_x at the each absorption peaks was deduced. The incident angle dependence of the A_y/A_x is represented in Eq. (1) [14].

$$\frac{A_y}{A_x}=\frac{2[\sin^2\theta+\sin^2\alpha(3\cos^2\theta-1)]-(3\cos^2\alpha-1)(3\cos^2\theta-1)\sin^2\gamma}{\sin^2\theta+(2-3\sin^2\theta)\sin^2\gamma} \quad (1)$$

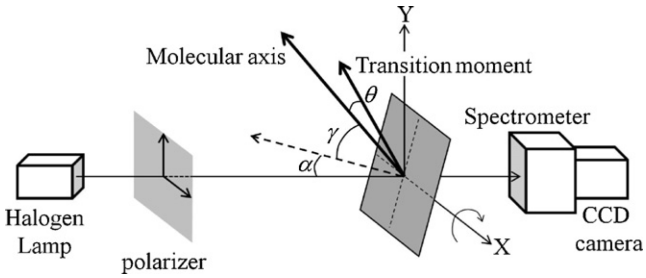

Fig. 2. Experimental setup for polarization dependence of absorption spectra.