Review

Durability of reversible photo-induced metal-to-semiconductor phase transitions on λ-Ti_3O_5

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INTRODUCTION

Optical discs commonly used as storage media, such as DVDs and Blu-ray Discs, employ chalcogenides as the recording material because chalcogenides exhibit photo-induced reversible changes. Although chalcogenides are extensively attractive materials possessing properties that are of interest in both fundamental and applied research, they are comprised of elements that are rare and expensive. Consequently, many studies are being conducted to find new materials suitable for next-generation optical storage media.

As part of these efforts, in 2010, our group successfully synthesized Ti_3O_5 nanoparticles with a unique phase, λ-Ti_3O_5, which exhibits a reversible photo-induced metal-semiconductor phase transition at room temperature.[1–3] Laser-light irradiation initiates a reversible transition between the black-colored metallic λ-Ti_3O_5 and the brown-colored semiconducting β-Ti_3O_5 (Fig. 1). λ-Ti_3O_5 is also an environmentally friendly and sustainable material because it is comprised of only highly abundant elements with large reserves. Due to these characteristics, λ-Ti_3O_5 has received increased attention as a promising candidate for use in rewritable recording media. In order for a recording material to be rewritable, it must be able to withstand numerous phase transition cycles. In this work, we report our findings on the durability of λ-Ti_3O_5 against repeated photoreversible phase transitions.

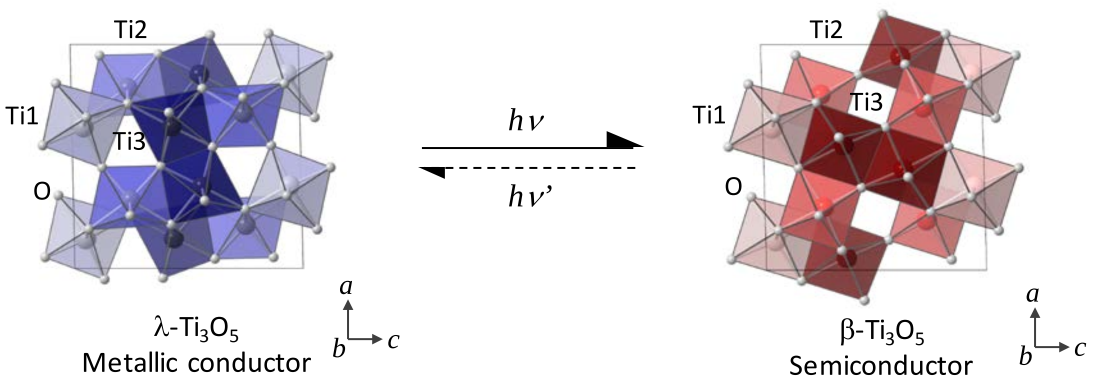

Figure 1. Reversible photo-induced metal-to-semiconductor phase transition of λ-Ti_3O_5 and β-Ti_3O_5.

EXPERIMENTAL SECTION

Figure 2 schematically depicts our experimental setup. The flake form of λ-Ti_3O_5 was formed into a pellet, and alternately irradiated by a nanosecond-pulsed laser light (532 nm, 8.8×10^{-6} mJ μm^{-2} pulse^{-1}) and a continuous wave (CW) semiconductor laser light (410 nm, 3.9×10^{-3} mW μm^{-2}). An optical microscope was used to record the color changes after each irradiation as images. The pulse laser, CCD, light sensor, and shutters were connected to a microcomputer. The microcomputer was connected to a computer, which controlled and automated the irradiation and image acquisition processes.

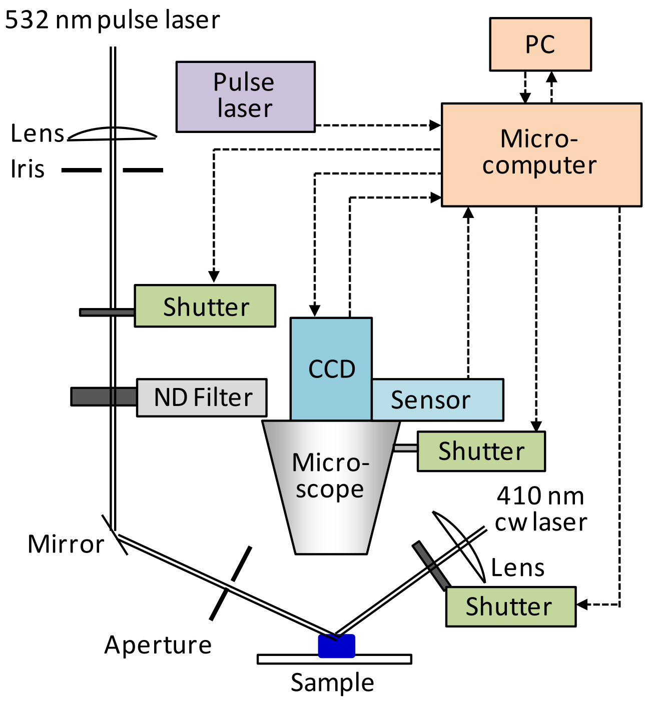

Figure 2. Schematic illustration of the experimental setup to evaluate the durability of reversible photo-induced phase transitions.

RESULTS

Reversible durability of photo-induced phase transition on λ-Ti_3O_5

The color changes of the λ-Ti_3O_5 sample after alternately irradiating with a 532 nm pulsed laser light and a 410 nm semiconductor laser light were examined. Before the light irradiation, λ-Ti_3O_5 was black. After irradiation with a 532 nm pulsed laser light, the irradiated area became brown, but subsequent irradiation with a 410 nm laser light restored the black color. This color change between black and brown was observed repeatedly on the sample upon further alternately irradiating with the 532 nm pulsed laser light and the 410 nm laser light. X-ray diffraction (XRD) measurements on the brown area showed the

XRD pattern of β-Ti_3O_5. Therefore, the observed color change between black and brown is due to the reversible photo-induced transition between λ-Ti_3O_5 and β-Ti_3O_5, respectively.

To quantify the color changes, RGB (Red-Green-Blue) color analysis was conducted on the obtained images, and the values of the three primary colors were obtained to characterize the two different phases in the photo-induced transition. Each image consisted of 40 × 65 pixels, and each pixel can store a maximum of 255 Red (R) components. (A pixel is the smallest unit of an image on a computer that contains information about color.) Histograms were created for each obtained image as shown in Figure 3a, where the horizontal axis represents the number of R components per pixel and the vertical axis represents the number of pixels in the image with the corresponding number of R components. The histograms show that the images of the brown area (β-Ti_3O_5) consisted mostly of pixels with 80 to 170 R components, whereas images of the black area (λ-Ti_3O_5) consisted mostly of pixels with 80 to 120 R components.

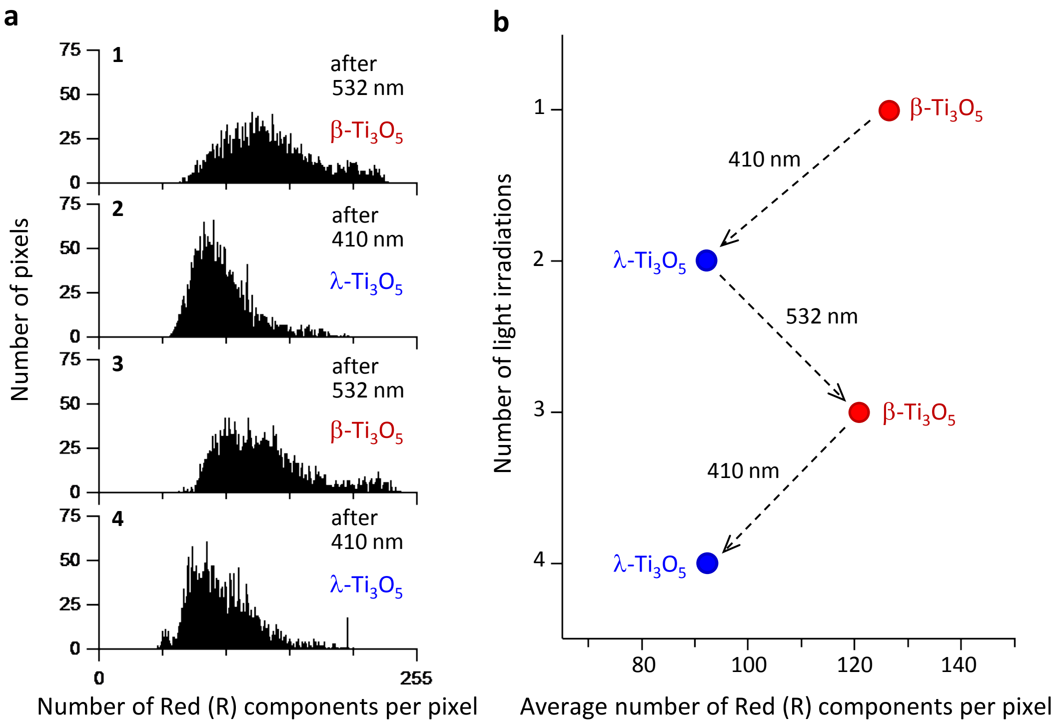

Figure 3. (a) Relationship between the number of Red (R) components per pixel and the number of pixels containing the corresponding number of R components in images after 532 nm and 410 nm laser-light irradiation. (b) Plot of the average number of R components per pixel.

Figure 3b illustrates the average number of R components per pixel in an image of the sample surface (55 × 90 μm^2) after each iteration of alternately irradiating with a 532 nm pulsed laser light and a 410 nm laser light. The clear alternation in the graph between two values of the average number of R components indicates that the reversible photo-induced phase transition between λ-Ti_3O_5 and β-Ti_3O_5 can be quantified.

We then proceeded to measure the durability of the photo-induced phase transition on λ-Ti_3O_5. We irradiated a sample up to 100 times and measured the changes in the number of R components and Blue (B) components per pixel after exposure to each alternating light. During the first three irradiations, some scatters were observed in the data, most likely due to changes in the roughness of the sample surface. However, after the fourth irradiation, the photo-induced phase transition occurred repeatedly with remarkable stability; no degradation was detected after 100 transitions.

SUMMARY

Herein we investigated the durability of reversible photo-induced metal-to-semiconductor phase transitions on λ-Ti_3O_5. RGB color analysis was used to quantify the photo-induced phase transitions from images of the sample surface taken by a microscope. We were able to confirm that λ-Ti_3O_5 exhibits a reversible photo-induced phase transition with good stability over numerous cycles (100 phase transitions). The observed stability is important property for applications. In the future, we plan to test more than 1000 phase transitions, and to rigorously assess the durability of λ-Ti_3O_5 under various applicative conditions.

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