Large reversible upconversion luminescence modification and 3D optical information storage in femtosecond laser irradiation-subjected photochromic glass

Daiwen Xiao^{1†}, Xiongjian Huang^{2†}, Yangke Cun¹, Zhen Hu¹, Zan Xu¹, Xue Bai¹, Yingzhu Zi¹, Lixiang Fu¹, Asif Ali Haider¹, Jianbei Qiu¹, Zhiguo Song¹, Guoping Dong^{2*} and Zhengwen Yang^{1*}

ABSTRACT Fast response, high luminescence contrast, three-dimensional (3D) storage, and nondestructive reading are key factors for the optical storage application of photochromic materials. Femtosecond (fs) laser direct writing technology with multiphoton nonlinear absorption is becoming a useful tool for microprocessing functional units in the 3D space of glass owing to its remarkable advantages, such as a fast processing speed and high processing accuracy. Herein, the photochromism of transparent glass codoped with rare-earth ions was investigated under 800-nm fs laser irradiation, affording a fast response. The photochromic glass achieves an upconversion luminescence (UCL) modification of 92%. The photochromic glass can be bleached back to its original color using heat treatment. The transmittance and UCL modification show excellent reproducibility under alternating stimulations between 800-nm fs laser irradiation and heat treatment. The data can be written in the interior of the transparent photochromic glass using 800-nm fs laser irradiation, facilitating 3D information storage. These results suggest that the 800-nm fs laser irradiation-subjected photochromic glass is an ideal optical data storage medium.

Keywords: three-dimensional optical storage, glass, upconversion luminescence, reversible modification, nondestructive reading

INTRODUCTION

With the rapid increase in digitalized information, digitalized information storage in a reliable, safe, long-life, and low-cost manner is essential. Replacing the traditional magnetic data storage technology, the current optical storage technology with low energy consumption, low cost, and high storage capacity has attracted considerable attention [1–3]. However, the latter experiences a challenge in storage capacity improvement because of the optical diffraction limitation [4,5]. Therefore, the exploration of novel optical information storage media and technology is important [6–8]. Photochromic materials with absorption and photoluminescence modulation were recently developed as novel optical data storage media [9–11]. As

established guiding rules for the optical storage application of photochromic materials, a fast photoresponse, large storage capacity, nondestructive reading, and high coloration and luminescence contrast are required [12,13]. Inorganic photochromic materials have garnered extensive attention as optical information storage media owing to their high strength or mechanical resistance, good thermal and chemical stabilities, and low environmental toxicity [14–16]. At present, many inorganic photochromic ceramics, such as BaMgSiO₄, Na_{0.5}Bi_{4.5}-Ti₄O₁₅, and PbWO₄, have been developed as optical data storage media, achieving the maximum downshift luminescence contrast of 96.3% [12,17–27]. However, the three-dimensional (3D) storage of optical information cannot be realized using photochromic ceramics, limiting their storage capacity. Unlike opaque bulk ceramics, 3D optical storage can be relatively easily realized using transparent bulk glass [28]. Photochromic glass doped with rare-earth ions was recently developed. The photochromic glass obtained under 473-nm laser irradiation for 10 min exhibited a downshift luminescence modulation of 68%, lower than that achieved by photochromic ceramics (96.3%) [29]. Thus, the low luminescence contrast and long response time of photochromic glass have restricted its applications. Therefore, developing a novel transparent photochromic glass with fast response and high coloration contrast and luminescence modification as the optical storage media is important.

Nondestructive reading capability is crucial for the successful application of optical storage devices [30,31]. An upconversion luminescence (UCL)-modified glass doped with rare-earth ions can convert two or more photons with low energy into one photon with high energy [32–35]. Compared with downshift luminescence, UCL with a large anti-Stokes shift overcomes overlapping shortcomings between the UCL and excitation spectra of rare-earth ions, achieving nondestructive reading, which was recently reported in photochromic ceramics based on the UCL modification [36]. However, reports on the reversible UCL modification and optical information storage application of transparent photochromic glass are unavailable. Recently, femtosecond (fs) laser is becoming a useful tool for constructing novel photonic devices, such as optical waveguides, photonic crystals, and microgratings, affording a fast processing speed

¹ College of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

² State Key Laboratory of Luminescent Materials and Devices, School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

[†] These authors contributed equally to this work.

* Corresponding authors (emails: yangzw@kmust.edu.cn (Yang Z); dgp@scut.edu.cn (Dong G))

and high processing accuracy [37–40]. The precise machining and information writing in the 3D space of the microregion of transparent glass can be realized using the multiphoton non-linear absorption of fs laser [37,41]. Herein, the photochromism of glass doped with rare-earth ions was investigated using the 800-nm fs laser direct writing technology, exhibiting fast and excellent photochromism. A photochromism reaction induced by the high UCL modification (92%), which is higher than the maximum UCL modification reported in the case of photochromic ceramics [42], is observed in the photochromic glass. Optical nondestructive reading is achieved based on the UCL modification under 980-nm laser excitation. The data can be written in the interior of a transparent glass using 800-nm fs laser irradiation, facilitating 3D information storage. The result suggests that the photochromic glass with high UCL modification and nondestructive reading shows potential as an optical data storage medium.

EXPERIMENTAL SECTION

Sample preparation

Borophosphate tellurite tungstate glasses were fabricated using different composites: $25\text{B}_2\text{O}_3\text{-}25\text{NaH}_2\text{PO}_4\text{-}10\text{TeO}_2\text{-(}35\text{-}x\text{)WO}_3\text{-}5\text{Na}_2\text{CO}_3\text{-}x\text{Sb}_2\text{O}_3$ ($x = 0, 1, \text{ and } 2 \text{ mol\%}$), $25\text{B}_2\text{O}_3\text{-(}24.7\text{-}y\text{)NaH}_2\text{PO}_4\text{-}10\text{TeO}_2\text{-}34\text{WO}_3\text{-}5\text{Na}_2\text{CO}_3\text{-}1\text{Sb}_2\text{O}_3\text{-}0.3\text{Yb}_2\text{O}_3\text{-}y\text{Er}_2\text{O}_3$ ($y = 0, 0.05, 0.1, 0.15, \text{ and } 0.20 \text{ mol\%}$), and $25\text{B}_2\text{O}_3\text{-(}24.9\text{-}z\text{)NaH}_2\text{PO}_4\text{-}10\text{TeO}_2\text{-}34\text{WO}_3\text{-}5\text{Na}_2\text{CO}_3\text{-}1\text{Sb}_2\text{O}_3\text{-}0.1\text{Er}_2\text{O}_3\text{-}z\text{Yb}_2\text{O}_3$ ($z = 0.1, 0.2, 0.3, 0.4, \text{ and } 0.50 \text{ mol\%}$). For this, stoichiometric raw materials (B_2O_3 , NaH_2PO_4 , TeO_2 , WO_3 , Na_2CO_3 , Yb_2O_3 , Er_2O_3 , and Sb_2O_3) were mixed homogeneously and melted in a furnace at 1050°C for 1 h in air. The melted solution was poured into a brass mold and cooled to room temperature (about 25°C), affording borophosphate tellurite tungstate glasses codoped with various concentrations of Yb^{3+} and Er^{3+} . The glasses were cut into a suitable size (length, width and height were 10, 10, and 3 mm, respectively) and polished after removing the internal stress using heat treatment. The photochromism of the borophosphate tellurite tungstate glasses was investigated under 800-nm fs laser (31 W cm^{-2}) irradiation for various times, and the spot size of the 800-nm fs laser was $\sim 3 \text{ mm}$. The photochromic glasses were bleached under thermal stimulation at different temperatures for various times.

Sample characterization

X-ray diffraction (XRD) patterns of the borophosphate tellurite tungstate glasses before and after 800-nm fs laser irradiation treatment were recorded on a D8 ADVANCE X-ray powder diffractometer (Bruker, Germany). The UCL spectra of the borophosphate tellurite tungstate glasses were measured under 980-nm laser excitation (HITACHI U-F-7000). The transmission spectra of the borophosphate tellurite tungstate glasses before and after 800-nm fs laser irradiation treatment were measured on a U-4100 spectrophotometer. The electron paramagnetic resonance (EPR) spectra of the raw, photochromic, and bleached glasses were recorded at room temperature. The elemental distribution of the glasses before and after 800-nm fs laser irradiation treatment was observed using scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDS). The valence states of W and Sb in the raw, photochromic, and bleaching glasses were analyzed using X-ray photoelectron spectroscopy (XPS). The fs laser system, which shows no specific

type, was provided by Spectra-Physics. The system comprised a seed light and an amplification stage. The pulse energy, frequency, and length of the fs laser were 0.02 J, 1000 Hz, and 37 fs, respectively. The optical microscopic images of the glasses were captured using a (Nikon AZ100M) optical microscope equipped with a camera. The photochromic and UCL images were obtained using a complementary metal-oxide-semiconductor (CMOS) sensor camera (Nikon D7100, Japan) under daylight and 980-nm laser excitation, respectively.

RESULTS AND DISCUSSION

The as-prepared $25\text{B}_2\text{O}_3\text{-}24.6\text{NaH}_2\text{PO}_4\text{-}10\text{TeO}_2\text{-(}35\text{-}x\text{)WO}_3\text{-}5\text{Na}_2\text{CO}_3\text{-}x\text{Sb}_2\text{O}_3\text{-}0.3\text{Yb}_2\text{O}_3\text{-}0.1\text{Er}_2\text{O}_3$ ($x = 0, 1, \text{ and } 2 \text{ mol\%}$) glasses were termed WBP-Sb0, WBP-Sb1, and WBP-Sb2. Fig. S1a presents the images and transmission spectra of the WBP-Sb0, WBP-Sb1, and WBP-Sb2 glasses, showing that the transparency of the glasses was associated with the addition of Sb_2O_3 . Compared with the WBP-Sb1 and WBP-Sb2 glasses, the WBP-Sb0 glass without Sb_2O_3 exhibited relatively low transmittance. The transmittance of WBP-Sb1 and WBP-Sb2 increased considerably after the addition of 1 or 2 mol% Sb_2O_3 in the glass composition, affording transparent glasses. The transmittance of the glasses was independent on the Sb_2O_3 concentration (Fig. S1a). Thus, the Sb_2O_3 concentration of 1 mol% was selected for subsequent analysis. Fig. S1b, c show the XPS spectra of W in WBP-Sb0 and WBP-Sb1, respectively. The XPS image of WBP-Sb0 revealed two peaks (35.9 and 37.9 eV) of W^{6+} and two peaks (34.8 and 36.8 eV) of W^{5+} . Notably, the peaks (34.8 and 36.7 eV) of W^{5+} in the XPS image of WBP-Sb1 decreased considerably after the addition of Sb_2O_3 (Fig. S1b, c). The polaron hopping between W^{6+} and W^{5+} afforded the coloration of WBP-Sb0 [43]. The addition of Sb_2O_3 in WBP-Sb1 limited the conversion from W^{6+} to W^{5+} . Thus, the transparent WBP-Sb1 glass was obtained. Glasses codoped with various concentrations of Yb^{3+} and Er^{3+} were prepared. The influence of Yb^{3+} or Er^{3+} concentrations on the UCL intensity and transparency of glass was also investigated. All glasses exhibited a green UCL at 524 and 548 nm and a red UCL at 658 nm under 980-nm laser excitation (Fig. S2a–d). The optimal concentrations of Er^{3+} and Yb^{3+} in the glass were approximately 0.1 and 0.3 mol%, respectively. The logarithmic relation between the 980-nm laser power and the UCL intensity of WBP-Sb1 (Fig. S3a) showed that the UCL at 524/548 and 658 nm corresponded to three- and two-photon processes, respectively, under 980-nm laser excitation; the possible UCL mechanism is proposed in Fig. S3b.

The photochromism of WBP-Sb1 was realized using 800-nm fs laser direct writing technology (Fig. 1a). The fixed 800-nm fs laser was focused on the glass sample, and the glass could be moved by controlling the optical microscope platform. The 2D and 3D photochromic patterns can be written on the surface and in the interior of the glasses, respectively (Fig. 1a). Fig. 1b shows the transmission spectra and images of WBP-Sb1 subjected to 800-nm fs laser (31 W cm^{-2} , spot size 3 mm) irradiation for various times. The transmittance and coloration of WBP-Sb1 changed after the glass was subjected to 800-nm fs laser irradiation. The transmittance of WBP-Sb1 decreased with an increase in the 800-nm fs laser irradiation time, and the glass became dark blue. The transmittance and coloration of the glass stabilized when the 800-nm fs laser irradiation time exceeded 15 s. Thus, the appropriate 800-nm fs laser irradiation time was

Figure 1 (a) Schematic of the writing and erasing of optical information. 2D and 3D photochromic patterns are recorded on the surface and in the interior of the glass, respectively, and the photochromic patterns can be erased using heat treatment. (b) Transmission spectra and images of the WBP-Sb1 glass subjected to 800-nm fs laser irradiation for various times. (c) Transmission spectra of the photochromic WBP-Sb1 glass subjected to 800-nm fs laser irradiation after thermal stimulation for 10 min at various temperatures. (d) The 548-nm transmittance of the WBP-Sb1 glass under alternating stimulations between 800-nm fs laser irradiation and heat treatment (300°C, 10 min) as a function of the number of cycles.

set as 15 s. The transmittance contrast (ΔR) of WBP-Sb1 was calculated using the equation $\Delta R = R_0 - R_1$, where R_0 and R_1 represent the transmittance before and after 800-nm fs laser irradiation, respectively. Fig. S4 shows that the 400–1600-nm transmission of WBP-Sb1 was modulated and the maximum ΔR value was ~33% after 800-nm fs laser irradiation for 15 s. These results demonstrate that a photochromic glass with a fast response was obtained under 800-nm fs laser irradiation, which is advantageous for optical storage applications.

The bleaching of the photochromic WBP-Sb1 glass induced by 800-nm fs laser irradiation was investigated under thermal stimulation at various temperatures for 10 min (Fig. 1c). The transmittance of WBP-Sb1 increased with the stimulation temperature. The transmittance intensity of this glass returned to its original state when the stimulation temperature reached 300°C. Fig. S5 presents the transmission spectra of the photochromic WBP-Sb1 glass treated for various times at 200°C. The transmittance of the photochromic WBP-Sb1 glass increased with the stimulation time and was restored to its primitive state when the stimulation time was 2 h. Fig. 1d shows the 548-nm transmittance of WBP-Sb1 achieved under alternating stimulations between 800-nm fs laser irradiation and 300°C heat treatment (10 min) as a function of the number of cycles. The photochromic WBP-Sb1 glass showed excellent rewritability and erasability.

Currently, several models have been proposed to explain the photochromism mechanism of materials. Reports indicate that the photochromism of WO_3 films is related to the formation of $\text{H}_x\text{W}_x^{6+}\text{W}_{1-x}^{5+}\text{O}_3$ [44–46]. The polarons hopping between W^{6+} and $\text{W}^{5+}/\text{W}^{4+}$ afford the photochromism of PbWO_4 ceramics. Fig. S6a presents the XRD patterns of WBP-Sb1 before and after 800-nm fs laser irradiation treatment. The XRD peaks were not detected, and the amorphous phase of WBP-Sb1 before and after 800-nm fs laser irradiation treatment was observed. Fig. S6b shows the normalized Raman spectra of WBP-Sb1 before and after 800-nm fs laser irradiation treatment induced by the 800-nm fs laser irradiation. The identical Raman spectra of WBP-Sb1 before and after 800-nm fs laser irradiation treatment suggested that the WBP-Sb1 glass structure before and after 800-nm fs laser irradiation treatment remained the same. Oxygen vacancy peaks were not detected in the room-temperature EPR spectra of the raw and photochromic WBP-Sb1 glasses (Fig. S6c). EDS mapping revealed the uniform distribution of all elements in WBP-Sb1 before and after 800-nm fs laser irradiation treatment, and element migration was not observed (Figs S7 and S8). Thus, the 800-nm fs laser irradiation-induced photochromism of WBP-Sb1 was not attributed to the glass crystallization, structural change, oxygen vacancy formation, and element migration [47]. The glass without the codoping of Yb^{3+} and Er^{3+} was

subjected to 800-nm fs laser irradiation for 15 s, exhibiting the same transmittance, in contrast to the WBP-Sb1 glass codoped with Yb^{3+} and Er^{3+} (Fig. S9). The XPS spectra of Yb^{3+} and Er^{3+} in WPB-Sb1 before and after 800-nm fs laser irradiation treatment showed no changes (Fig. S10). This result demonstrates that the photochromism of WBP-Sb1 was unrelated to codoping using Yb^{3+} and Er^{3+} after 800-nm fs laser irradiation. Fig. 2a–d present the XPS spectra of W and Sb in WPB-Sb1 before and after 800-nm fs laser irradiation treatment. Compared with WPB-Sb1 before photochromism (Fig. 2a), the peaks of W^{5+} located at 34.7 and 36.8 eV increased after photochromism (Fig. 2c). Two peaks of Sb^{3+} were detected at 530.7 and 540.1 eV in WPB-Sb1 before photochromism, and no XPS peak of Sb^{5+} was observed before

photochromism (Fig. 2b). Two XPS peaks of Sb^{5+} were detected at 531.2 and 540.6 eV after photochromism (Fig. 2d) [48]. The 800-nm fs laser irradiation with high energy may induce the ionization of Sb^{3+} , resulting in the conversion of Sb^{3+} to Sb^{5+} and the production of free electrons [49]. Free electrons were captured by W^{6+} in the glass, yielding W^{5+} . The electrons localized around W^{5+} could “facilitate the polarization of the surrounding lattice, forming small polarons”. The light stimulation could afford the mutual transition of polarons between two or three types of ions with different valence states, inducing light absorption. The reactions $\text{Sb}^{3+} + h\nu \rightarrow \text{Sb}^{5+} + 2e^-$ and $2\text{W}^{6+} + h\nu + 2e^- \rightarrow 2\text{W}^{5+}$ may occur in the case of WBP-Sb1 after 800-nm fs laser irradiation. The hopping of polarons between W^{6+} and

Figure 2 XPS spectra of (a) W and (b) Sb in the WBP-Sb1 glass before photochromism. XPS spectra of (c) W and (d) Sb in the photochromic (PC) WBP-Sb1 glass subjected to 800-nm fs laser irradiation for 15 s. XPS spectra of (e) W and (f) Sb in the decolored (DC) WBP-Sb1 glass stimulated at 300°C for 10 min.

W⁵⁺ induced the photochromism of WBP-Sb1 [50–52].

The photochromic WBP-Sb1 glass subjected to 800-nm fs laser irradiation for 15 s was bleached at 300°C for 10 min. The XPS spectra of rare-earth ions and the XRD pattern, Raman spectra, and EPR spectra of the bleached WBP-Sb1 glass revealed that the glass structure, amorphous phase, oxygen vacancy, and valence state of rare-earth ions showed no change after thermal stimulation, contrary to the photochromic WBP-Sb1 glass (Figs S6 and S10). The XPS spectra of W and Sb in the bleached WBP-Sb1 glass (300°C for 10 min) are presented in Fig. 2e, f, respectively. Compared with the photochromic WBP-Sb1 glass (Fig. 2c), the peaks of W⁵⁺ at 34.7 and 36.8 eV decreased after thermal bleaching. The two XPS peaks of Sb⁵⁺ at 531.2 and 540.6 eV disappeared. W⁵⁺ was oxidized to W⁶⁺ in air after thermal stimulation, and Sb⁵⁺ was reduced to Sb³⁺. In the case of the photochromic WBP-Sb1 glass, the reactions $2W^{5+} \rightarrow 2W^{6+} + 2e^-$ and $Sb^{5+} + 2e^- \rightarrow Sb^{3+}$ occurred after thermal stimulation. Thus, the thermal bleaching of the photochromic WBP-Sb1 glass was realized.

Photochromism and UCL were observed in the case of WBP-Sb1. The UCL of WBP-Sb1 can be modulated based on its photochromic reaction. Fig. 3a presents the UCL spectra of WBP-Sb1 subjected to 800-nm fs laser irradiation for various times after 980-nm laser excitation. The UCL intensity of the photochromic WBP-Sb1 glass decreased when the 800-nm fs laser irradiation time was increased, exhibiting photochromism-induced UCL modification. The equation $\Delta R_m = (R_0 - R_L)/R_0 \times 100\%$ was used to characterize the degree of UCL modulation, where R_0 and R_L are the 548-nm UCL intensity of the as-prepared and photochromic glasses, respectively. As expected, the degree of UCL modulation increased with the 800-nm fs laser

irradiation time. The maximum UCL modification of WBP-Sb1 was ~92% when the 800-nm fs laser irradiation time reached 15 s (Fig. 3b). The highest degree of luminescence modification was 70% lower than that of the photochromic glass. The 92% UCL modification of the photochromic WBP-Sb1 glass after 800-nm fs laser irradiation is higher than the maximum luminescence modification reported for the photochromic glass [29]. The photochromic WBP-Sb1 glass subjected to 800-nm fs laser irradiation was bleached and exposed to heat treatment at various temperatures for 10 min, and the corresponding UCL spectra are shown in Fig. 3c. The UCL intensity of the bleached WBP-Sb1 glass increased with the heat treatment temperature. The UCL recovery degree (ΔR_r) was characterized using the equation $\Delta R_r = R_b/R_0 \times 100\%$, where R_0 and R_b are the 548-nm UCL intensity of the as-prepared and decolored WBP-Sb1 glasses, respectively. The ΔR_r value of the decolored WBP-Sb1 glass was ~99% when the stimulation temperature reached 300°C, and the UCL reversion of the decolored WBP-Sb1 glass was realized (Fig. 3d). The influence of the stimulation time at 200°C on the decoloration and UCL reversion of the photochromic glass were also observed (Fig. S11). The UCL of the photochromic WBP-Sb1 glass recovered to its initial state when the stimulation time was 2 h. Fig. 3e presents the 548-nm UCL intensity of WBP-Sb1 under alternating stimulations between 800-nm fs laser irradiation and 300°C heat treatment for 10 min after 980-nm laser excitation, showing no UCL deterioration. The reversible UCL modification of WBP-Sb1 was also realized. These results suggest that the photochromic glass with a high UCL modification shows potential applications as optical data storage media.

The UCL decay lifetime of WBP-Sb1 before and after 800-nm

Figure 3 (a) UCL spectra and (b) degree of UCL modulation (ΔR_m) of the WBP-Sb1 glass subjected to 800-nm fs laser irradiation for various times after 980-nm laser excitation. (c) UCL spectra and (d) recovery degree (ΔR_r) of the photochromic WBP-Sb1 glass subjected to heat treatment at various temperatures for 10 min. (e) The 548-nm UCL intensity of WBP-Sb1 under alternating stimulations between 800-nm fs laser irradiation and 300°C heat treatment (10 min) as a function of the number of cycles. (f) Decay lifetime curves of the 548-nm intensity of the WBP-Sb1 glass subjected to 800-nm fs laser irradiation for various times.

fs laser irradiation treatment was measured to characterize the UCL modification mechanism. The UCL decay lifetime of the photochromic WBP-Sb1 glass subjected to 800-nm fs laser irradiation for various times showed no changes compared with that of the raw WBP-Sb1 glass (Fig. 3f).

The results demonstrate that the UCL modification of WBP-Sb1 was not attributed to the resonance energy transfer from Er^{3+} to the glass host. The absorption of the photochromic WBP-Sb1 glass overlapped with the UCL peaks of Er^{3+} . The UCL modification was ascribed to the absorption of the photochromic WBP-Sb1 glass host.

Simple optical information patterns and a complex 2D code can be written on the WBP-Sb1 glass surface using the 800-nm fs laser direct writing technology (Fig. 4a). The information “Kunming University of Science and Technology Official Website” (KUST) could be read out using a smartphone to scan the image of the 2D code. The information readout by scanning the 2D code using a smartphone at any time is consistent with the website content, realizing real-time updates of information (Supplementary Video 1). The encoded binary arrays corresponding to the “KUST” alphabets were written on the WBP-Sb1 glass surface using 800-nm fs laser irradiation. Moreover, the encoded binary arrays corresponding to the “KUST” alphabets could be rewritten on the WBP-Sb1 glass surface using 800-nm fs laser irradiation after erasing the encoded binary arrays under 300°C thermal stimulation for 10 min (Fig. 4b). The UCL pattern on the WBP-Sb1 glass surface could also be realized after 980-nm laser excitation based on the UCL modification induced by the photochromic reaction (Fig. 4c). The photochromic dot arrays were patterned on the WBP-Sb1 glass surface, which was subjected to 800-nm fs laser irradiation for 15 s. Weak UCL spectra of the photochromic dots were detected

after the 980-nm laser excitation, and intense UCL spectra were observed in other regions without photochromism. The UCL modification spectra corresponded to the binary states of “0” and “1” (Fig. 4d), realizing the nondestructive reading of bit-by-bit UCL signals. Furthermore, the photochromism patterns and UCL modification were observed in the case of the glass codoped with Yb^{3+} and Tb^{3+} after the 800-nm fs laser irradiation (Fig. S12), which are independent of the doping species of rare-earth ions. This result suggests that the photochromic WBP-Sb1 glass doped with rare-earth ions is an ideal optical storage medium.

Unlike photochromic films and ceramics, the data could be written in the interior of the transparent WBP-Sb1 glass using the 800-nm fs laser irradiation. Three rectangles with different sizes and Chinese characters “three”, “four”, and “five” were written in the interior of various layers of the glass by the focused 800-nm fs laser (143 kW cm^{-2} , spot size $3 \mu\text{m}$) using the direct writing technology, which could be detected by employing an optical microscope (Fig. 5a). The Chinese characters in the interior of various layers of the glass were clearly and hierarchically read out using an optical microscope (Supplementary Video 2). The entire 3D pattern could be microprocessed in the glass interior using the 800-nm fs laser irradiation (Fig. 5b), affording 3D information storage.

Other continuous lasers, such as those at 808 (78 W cm^{-2}), 690 (42 W cm^{-2}), 532 (284 W cm^{-2}), or 473 nm (151 W cm^{-2}), were used to irradiate WBP-Sb1. No photochromism of WBP-Sb1 was observed under 808-nm (78 W cm^{-2}), 690-nm (42 W cm^{-2}), or 532-nm (284 W cm^{-2}) continuous laser irradiation for 15 min (Fig. S13). However, WBP-Sb1 showed photochromism under 473-nm (151 W cm^{-2}) continuous laser irradiation for 15 min, and the photochromism reached

Figure 4 (a) Photochromic pattern information, digital information, and raw and enlarged photochromic 2D code pattern. (b) Encoded binary arrays recorded using 800-nm fs laser; binary arrays erased by 300°C heat treatment for 10 min, and corresponding binary code rewritten using 800-nm fs laser. (c) Photochromic and UCL patterns after 980-nm laser excitation. (d) Photochromic dot arrays patterned on the WBP-Sb1 glass surface and the 548-nm UCL spectra of the corresponding photochromic dot arrays after 980-nm laser excitation; the weak UCL spectrum is from the photochromic dots, and the intense UCL spectrum is from the other region without photochromism. Scale bar: 5 mm.

Figure 5 (a) Optical microscopic images of three rectangles with different sizes and Chinese characters “three”, “four”, and “five” recorded in various layers of the glass; (b) 3D pattern in the interior of the transparent glass from top and front views in daylight.

saturation when the 473-nm continuous laser irradiation time reached 15 min (Fig. S14a). The maximum ΔR value was $\sim 9.5\%$ (Fig. S14b), lower than that obtained using the 800-nm fs laser irradiation (33%). Fig. S15a, b present the UCL spectra and degree of UCL modulation of the photochromic WBP-Sb1 glass subjected to 473-nm continuous laser irradiation. The maximum UCL modification of WBP-Sb1 was 68% under the 473-nm continuous laser irradiation time of 15 min, lower than that obtained under the 800-nm fs irradiation time of 15 s (92%). Thus, these results demonstrate that a photochromic glass with high coloration contrast, good luminescence modification, and fast response was obtained under 800-nm fs laser irradiation, which is advantageous for optical storage applications.

CONCLUSIONS

Overall, the fast response and excellent photochromism of the UCL glass doped with rare-earth ions were realized using the 800-nm fs laser direct writing technology. The photochromic glass exhibited excellent rewritability and erasability under alternating stimulations between 800-nm fs irradiation and heat treatment. The maximum UCL modification (92%) of the glass doped with rare-earth ions was achieved after 980-nm laser excitation based on the photochromism reaction. The 2D code was designed and recorded on the glass surface using the 800-nm fs laser direct writing technology, realizing the real-time update of information by scanning the 2D code using a smartphone. The data could be written in the interior of the transparent glass using the 800-nm fs laser irradiation, facilitating 3D information storage. The results suggest that the photochromic glass with high UCL modification and nondestructive reading shows potential applications in the fields of high-capacity optical data storage and information security.

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Author contributions Yang Z and Dong G conceived, designed, and supervised the overall project. Xiao D and Huang X performed the experiments. All the authors discussed the results and commented on the manuscript.

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Supplementary information Supporting data are available in the online version of the paper.

Daiwen Xiao is currently a graduate student at Kunming University of Science and Technology under the supervision of Prof. Zhengwen Yang. His current interest includes the fabrication of photochromic glass for optical storage applications.

Zhengwen Yang is currently a professor at the College of Materials Science and Engineering, Kunming University of Science and Technology. He obtained his bachelor's degree in 2002 and master's degree in 2005 from Jilin University, respectively. He received his PhD degree from Tsinghua University in 2009. His research interests include the modification and enhancement of upconversion luminescence.

飞秒激光辐照诱导光致变色玻璃中的上转换发光可逆调控和3D光学信息存储

肖代文^{1†}, 英雄健^{2†}, 寸阳珂¹, 胡振¹, 徐赞¹, 白雪¹, 字映竹¹, 付丽香¹, Asif Ali Haider¹, 邱建备¹, 宋志国¹, 董国平^{2*}, 杨正文^{1*}

摘要 快速响应、高发光对比度、三维存储和信息无损读取是光致变色材料光存储应用的几个关键因素。具有多光子非线性吸收的飞秒激光直写技术以其加工速度快、加工精度高等独特优势，正成为玻璃三维空间微加工功能单元的有效工具。本工作研究了800 nm飞秒激光照射下稀土离子掺杂透明玻璃的光致变色性质，结果证实800 nm飞秒激光辐照下玻璃展现了快速光致变色响应。在光致变色玻璃中实现了92%的上转换发光调控。光致变色玻璃可通过热刺激漂白回原色，在800 nm飞秒激光辐照和热处理交替刺激下，光致变色玻璃的透射率和上转换调控表现出良好的重现性。通过800 nm飞秒激光照射，可将数据信息写入透明玻璃内部，实现三维信息存储。结果表明，800 nm飞秒激光辐照诱导的光致变色玻璃是理想的光学数据存储介质。