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Optical switch and luminescence properties of sol–gel hybrid organic–inorganic materials containing azobenzene groups and doped with neodymium ions

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ABSTRACT TiO_2/γ-glycidoxypropyltrimethoxysilane and methyltrimethoxysilane hybrid organic–inorganic material, which contains azobenzene groups and is doped with neodymium ions, was prepared by a low temperature sol–gel technique. The trans-cis-trans photoisomerization cycles of the hybrid film were investigated by a photoirradiation with UV light followed by visible light. An intense room-temperature upconversion emission at 397 nm was also measured from a hybrid film heated at a low temperature of 80 °C upon excitation with a xenon lamp at a wavelength of 580 nm. The mechanism of the upconversion is proposed and indicates that the sequential two-photon absorption process originating from the long-lived $^4F_{3/2}$ excited state should be responsible for the up-conversion process. These results indicate that the prepared hybrid materials with multifunctional photonic properties are promising candidates for integrated optics and photonic applications, which would allow directly integrating onto a single chip, the upconversion device with the pump source, and optical data storage and optical switching devices.

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1 Introduction

There is an increasing interest in photonic applications due to a desire for improvement of devices for information storage, processing, displaying and transfer. The phenomenon of photoinduced anisotropy is one of the best candidates for this purpose. Photoinduced anisotropy causes optical dichroism and birefringence in various materials by generating an orientational order. Azobenzene-containing polymers have attracted considerable attention as photochromic and photorefractive materials for optical memories and optical switches due to the reorientation of azobenzene groups through photochemical trans-cis-trans isomerization cycles under photoirradiation [1–5]. Hence extensive studies have been made of azobenzene-based photochromic polymers and azobenzene-doped photorefractive materials, where low molecular-weight azobenzene compounds are dispersed in polymer binders [6–10], due to their potential applications in photonic-based materials.

The availability of high-power infrared laser diodes has stimulated research in the areas of upconversion pumped visible lasers and their potential applications in areas such as three-dimensional displays, high-density optical data reading and storage, infrared laser viewers and indicators [11–14]. In particular, recent spectroscopic results showed that neodymium could be a good candidate for upconversion fluorescence and laser applications [15, 16]. Therefore, there has recently been a considerable amount of interest in the up-conversion process of neodymium ions in various kinds of glass or crystal host materials [17–19]. Among the upconversion materials, bulk crystals, glasses, and fibers are quite attractive but the high cost associated with the material preparation and device packaging as well as not being integratable with semiconductors may limit their applications. Films, however, combine the advantages of the bulk materials and the compactness of fibers, offering good prospects for upconversion devices. Recently, optically homogeneous and transparent organic–inorganic hybrids containing organic components have been widely synthesized and reported. The introduction of organic groups into an inorganic network improves mechanical properties, leading to easier processing of thick films [20]. The modification of an inorganic network structure with organic groups gives a larger space for the isomerization of organic photoactive molecules as compared to inorganic glasses [21]. Therefore, organic–inorganic hybrids are thus anticipated as desirable materials for photonic applications, which can trap organic molecules. In particular, organic–inorganic hybrid waveguides in thin film configuration become more important, as they can be obtained at a low heat treatment temperature, which would allow direct integrating onto the same chip with the active device with the pump source and other optoelectronic components. The optical properties of neodymium ion doped sol–gel GeO_2/γ-glycidoxypropyltrimethoxysilane hybrid planar waveguides was reported in our previous work [22]. However, we think it is of greater interest and significance to study the doping of planar hybrid waveguides co-doped with neodymium ions and photochromic amorph-

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ous molecular materials based on azobenzene for multifunctional photonic applications, although there have not been any reports of preparation and photonic properties of such neodymium and azobenzene co-doped optical multifunction properties waveguide films so far. Here, we report the photoresponse and upconversion luminescence properties of TiO_2/γ-glycidoxypropyltrimethoxysilane and methyltrimethoxysilane hybrid materials codoped with neodymium ions and photochromic amorphous molecular materials based on monoazobenzene, 4-(4-hydroxybutyloxy)azobenzene.

2 Experimental

The preparation details of TiO_2/γ-glycidoxypropyltrimethoxysilane (GLYMO) and methyltrimethoxysilane (MTES) hybrid material sol, are described elsewhere [23]. Neodymium (Nd) was added as neodymium nitrate with a $Nd/(TiO_2 + GLYMO + MTES)$ molar concentration of 0.5 mol. % drop-by-drop into the TiO_2/(GLYMO-MTES) hybrid solution. The 4-(4-hydroxybutyloxy) azobenzene compound as azodye was added to the TiO_2/(GLYMO-MTES) sol–gel hybrid solution doped with neodymium in the weight ratio of 0.5% of the sol–gel hybrid solution. The final mixture was stirred for about 30 h at room temperature. We used quartz glass as substrates and they were ultrasonically cleaned in acetone and ethanol, respectively, rinsed with de-ionized water and dried in pure N_2 gas. Two layers of the sol–gel films were spun onto the substrate at 3000 rpm for 35 s. The details are as follows. Firstly, one layer of film was deposited onto the substrate and baked for 10 min at a low heat treatment temperature of 80 °C; and then the second layer was directly deposited onto the surface of the first layer film; finally, the film-coat was baked for about 10 min at 80 °C again.

The photo-responsive measurements of the hybrid films were carried out by a Shimadzu UV-2501 PC UV-visible (UV-vis) spectrophotometer after irradiation by UV light for various time intervals. The UV irradiation light was produced by a Driel Instrument 66901 500 W mercury lamp through a filter centered at 370 nm with a circular cooling water system to maintain the lamp temperature at about 5 °C. The UV irradiation light intensity was 2.0 mW/cm^2. The up-conversion emission spectrum of the hybrid films was measured on a Spex Fluorolog-3 spectrofluorometer with a 1934D3 phosphorimeter attached. The source of excitation in this measurement system is a continuous wavelength (cw) xenon lamp source for the steady state up-conversion emission measurement. The measured sample (film) was excited by the xenon lamp at an incidence angle of 45° and the up-conversion luminescence was collected at an angle of 45° to the sample. This system employs the Datamax software package to acquire the spectrum. The thickness of the hybrid film was also measured by an m-line apparatus (Metricon 2010) based on the prism coupling technique and a two-layer film with a thickness of approximately 2.46 μm can be easily obtained.

3 Results and discussion

Figure 1a and b show the UV-visible absorption spectra of the hybrid film after irradiation with non-polarized UV (370 nm) light, and subsequent irradiation with visible (410 nm) light. At room temperature, azobenzene chromophores are expected to be in the more stable trans state in the dark. It can be seen from the absorption spectra of Fig. 1a in the range of 300–600 nm that there is a major absorption peak at 352 nm and a weak one at 437 nm, which are related to the $\pi-\pi^*$ electronic transition of the trans isomers and the $n-\pi^*$ electronic transition of the cis isomers. When the hybrid film is irradiated by non-polarized UV light of 370 nm wavelength, azobenzene chromophores undergoes a trans-cis photoisomerization process. The intensity of the absorption peak at 352 nm gradually decreases with an increase of the irradiation time until an equilibrium state is reached. At the same time, the weak peak at 437 nm becomes more pronounced. The equilibrium or photostationary state is reached in about 120 s under the present irradiation conditions. Figure 1b shows that when the hybrid film is irradiated by visible light of 410 nm wavelength, azobenzene chromophores undergo a cis-trans photoisomerization process. The $\pi-\pi^*$ absorption of the trans isomers gradually increases and the $n-\pi^*$ absorption of the cis isomers decreases, showing a partial back-conversion of the absorption spectra. These results obtained from Fig. 1 indicate that irradiation of

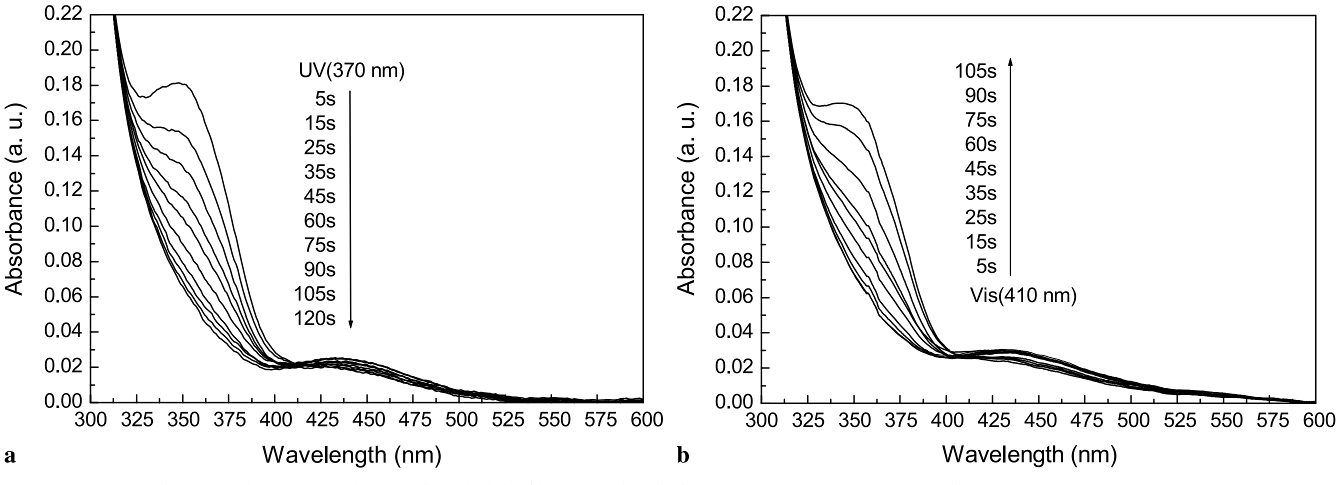

FIGURE 1 UV-vis absorption spectra change of the hybrid films upon irradiation. (**a**) at UV (370 nm), (**b**) at vis (410 nm)

the as-prepared hybrid film with 370 nm light at room temperature causes a decrease in the absorbance around 352 nm due to the photoisomerization of the trans-form to the cis-form. When irradiation ceased after the reaction system has achieved the photostationary state, the electronic absorption spectra of the hybrid film gradually recovered to the original one due to the backward isomerization from the cis-form to the trans-form by irradiation with 410 nm light.

The reversibility of the trans-cis photoirradiation of the hybrid films was studied by alternating irradiation of the non-polarized UV and visible light. The samples studied were dark-adapted before measurements and were then irradiated by UV light. After the photostationary state was reached, the samples were irradiated by visible light immediately until another photostatioary state was observed again. The process was repeated for at least three irradiation cycles. At the end of each irradiation, the $\pi-\pi^*$ absorption of the trans isomers, which correspond to the photostationary state, was recorded, and the results are shown in Fig. 2. It can be seen from the Fig. 2 that the trans-cis photoisomerization of the hybrid film shows a good reversibility within the irradiation cycle. Considering that the photostationary state reached by irradiation of the visible light is a mixture of the trans and cis isomers, the absorbance does not completely recover back to the original dark-adapted state due to the existence of the trans isomers only. It should be stressed here that there is no apparent loss of photo-reversibility over the cycles investigated as the absorbance is essentially independent of the irradiation cycles. In addition, it was also found that the isomerization process could be reversed thermally. When the irradiated samples were thermally heated at a certain temperature, the intensity of the absorption peak around 352 nm increased steadily, until reaching the starting value before the irradiation, thus confirming the reversibility of the photothermal cis-trans isomerization process. The results obtained from Fig. 2 indicate that the as-prepared hybrid film should be a good candidates for optical data storage and optical switching. The switching characteristic of the as-prepared hybrid film can be understood as a change in absorbance of the probe light passed through the irradiated region when they were illuminated at wavelengths to bring out the photoisomerization of the azobenzene. It can be seen from Fig. 2 that the change in the absorbance measured shows a function of time simultaneously when the hybrid film was irradiated alternately by non-polarized UV at 370 nm and visible light at 410 nm at room temperature, respectively. Thus the time dependence or the dynamics of "on"–"off" switching cycles of the as-prepared hybrid film is as follows. When the UV light is turned on, absorbance at the wavelength of 370 nm decreases during the first few seconds and reaches a final value at about 0.06 (similar to a "off" state of the switching). When the UV light is turned off and the visible light is turned on, the absorbance starts to increase and reaches an initial value of about 0.18 (similar to an "on" state of the switching). That is to say, the change of the absorbance of the hybrid film at the wavelength of 370 nm due to the photoirradiation from 0.18 to 0.06 and then from 0.06 to 0.18 is similar to the "on"–"off" switching cycles. As compared with the materials reported in [24, 25], it can be noted that the switching characteristic of the present hybrid film has a relatively long response time, and it is probably related to the photoresponsive measurement of the as-prepared hybrid film under irradiation of the non-polarized UV light, which is different from that reported in [24, 25] by an irradiation of the laser. Actually, it is also expected that a much shorter response time for the transition of the trans-cis-trans photoisomerization process can be reached by using a laser pulse irradiation source instead of the non-polarized UV light source [26, 27]

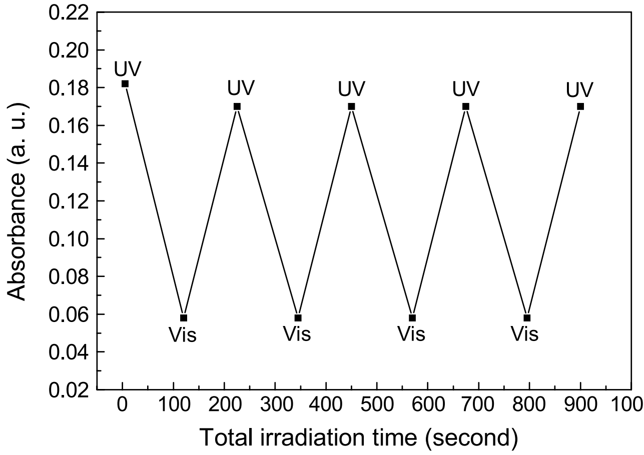

FIGURE 2 Reversible trans-cis photoisomerization of the hybrid film after irradiation with UV and visible light alternately (light intensity, UV: 2 mW/cm^2, vis: 3 mW/cm^2)

Figure 3a shows the visible up-conversion emission characteristic spectrum of radiation emanating from the hybrid film with a xenon lamp excitation at the wavelength of 580 nm. The absorption spectrum of the hybrid film, reveals an excitation transition of neodymium ion (Nd^{3+}) at 580 nm ($^4I_{9/2} \rightarrow {}^4G_{5/2}$), is shown in Fig. 3b, indicating that the neodymium ions have an intense absorption transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}$) at the 580 nm band and so it was chosen to measure the up-conversion emission spectrum of the hybrid film. It can be seen from Fig. 3 that there is a bright violet up-conversion emission transition at 397 nm corresponding to the $^4D_{3/2} \rightarrow {}^4I_{13/2}$ or $^2P_{3/2} \rightarrow {}^4I_{11/2}$ transitions of the neodymium ions. In addition, a relatively weak ultraviolet emission transition at 371 nm ($^4D_{3/2} \rightarrow {}^4I_{11/2}$ or $^2P_{3/2} \rightarrow {}^4I_{9/2}$) and a blue emission transition at 469 nm ($^4D_{3/2} \rightarrow {}^4I_{15/2}$ or $^2P_{3/2} \rightarrow {}^4I_{13/2}$) are also clearly observed. These results indicate that the upconversion luminescence transition spectrum of $^4D_{3/2} \rightarrow {}^4I_{J+1}$ or $^2P_{3/2} \rightarrow {}^4I_J$ ($J = 13/2$, $11/2$, $9/2$) is found to be essentially similar to those reported in [22, 28, 29]. It should be also mentioned that we know of no other intense upconversion luminescence at 397 nm from the neodymium (III) ion in a hybrid film heated at the low temperature of 80 °C as a result of being induced by a continuous wavelength xenon lamp. A relatively weak emission band centered at about 450 nm can be also observed, but no reasonable transition is assigned to the emission band. In order to understand this better, the host material of TiO_2/GLYMO-MTES hybrid film was also measured, but no up-conversion emission was observed in this range of wavelength, indicating that the emission at 450 nm is not related to the host material of TiO_2/GLYMO-MTES. As a consequence, we suspect that this emission is probably due to the

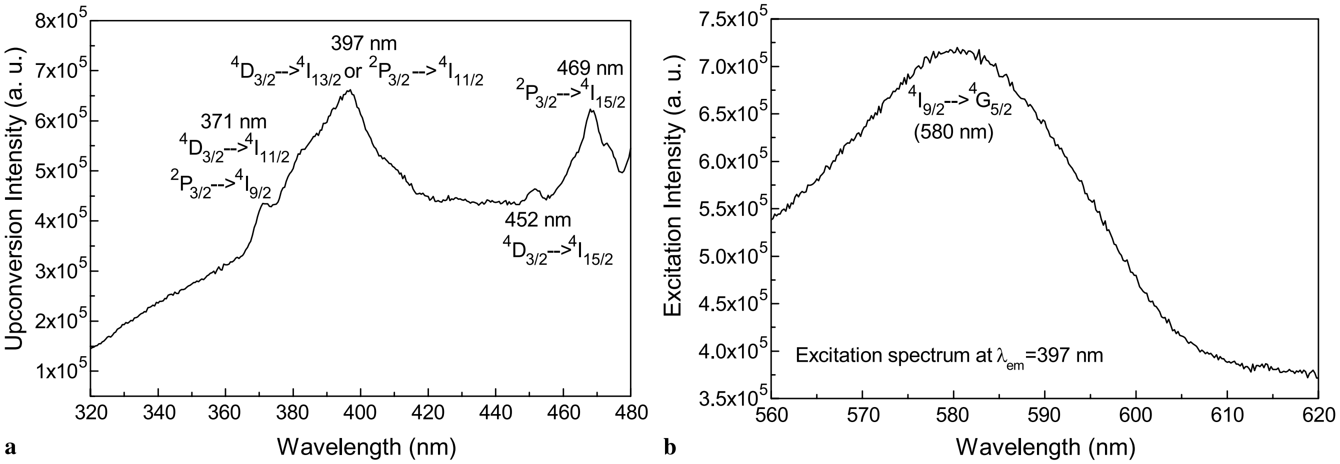

FIGURE 3 (**a**) Visible up-conversion emission spectrum from the hybrid film under excitation of 580 nm light, (**b**) excitation spectrum of the hybrid film with a xenon lamp

splitting of the emission corresponding to the $^4D_{3/2} \rightarrow {}^4I_{15/2}$ or $^2P_{3/2} \rightarrow {}^4I_{13/2}$ transitions of the neodymium ions, that is to say, the $^4D_{3/2} \rightarrow {}^4I_{15/2}$ or $^2P_{3/2} \rightarrow {}^4I_{13/2}$ transition splits into two peaks at 450 nm corresponding to the $^4P_{3/2} \rightarrow {}^4I_{13/2}$ transition and 469 nm corresponding to the $^2P_{3/2} \rightarrow {}^4I_{15/2}$ transition as reported in [30].

The above results and analysis indicate that the upconversion mechanism in our hybrid film includes the sequence of ground- and excited-state absorption steps [31, 32]. The observed up-conversion emission in Fig. 3 is simply due to the sequential two-photon absorption process. In this process, due to an initial absorption of a 580 nm photon, electrons from the ground state of $^4I_{9/2}$ first get excited to an upper state of $^4G_{5/2}$. Considering that the energy range between $^4G_{5/2}$ and $^4F_{3/2}$ contains several closely spaced intermediate levels, so this $^4G_{5/2}$ state is short-lived, and the excited population rapidly decays non-radiatively to the metastable $^4F_{3/2}$ state. Because this metastable state has a relative long lifetime and thus before the population decays further downwards, the electron has a high chance to absorb a second 580 nm photon and gets excited to the $^4D_{3/2}$ state. Afterwards, some populations will decay radiatively to the ^4I_J ($J = 11/2$, $13/2$, and $15/2$) states, resulting in certain relevant up-conversion emission transitions. The other populations will decay non-radiatively firstly onto the $^2P_{3/2}$ state, and then cause the other possible upconversion photon emissions at possible wavelengths.

4 Conclusions

In conclusion, a new hybrid material with valuable optical multifunctional properties, which include optical data storage, optical switching and upconversion luminescence, for photonic applications based on the doping of azobenzene and neodymium ions, has been prepared by the sol–gel process from an organic–inorganic hybrid system. We have also carried out a detailed analysis of the photoresponsive properties based on the trans-cis-trans photoisomerization process, and the visible up-conversion emission process from the hybrid films to verify their optical switching and luminescence performance. The results show that azobenzene can be incorporated into silicon oxide matrices using the same 4,4′-dihydroxyazobenzene as the starting materials by the sol–gel technique. The upconversion mechanism proposed is based on a sequential two-photon absorption process upon excitation with a yellow radiation at 580 nm from a xenon lamp source. The present study shows that the prepared hybrid materials, obtained at a low temperature of 80 °C, are promising candidate materials for multifunctional photonic applications.

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