Rewritable Optical Memory Through High-Registry Orthogonal Upconversion

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An experimental design, based on a combination of core–shell-structured upconversion nanoparticles and diarylethene photochromic molecules, for achieving rewritable optical memory is reported. This core–shell design enables the nanoparticles to emit two sets of distinct emission bands with ultrahigh spectral purity through laser excitation at 980 and 1532 nm. Importantly, the ultraviolet emission of the nanoparticles under 980 nm irradiation is used to activate the cyclization reaction of diarylethene through C–C bond formation, while the green emission from the nanoparticles upon 1532 nm excitation leads to the cleavage of the newly formed C–C bond. This pathway offers a convenient and versatile optical method for controlling the process of data writing and erasing with high spatiotemporal resolution.

In recent years considerable attention has been paid to photochromic materials due to their potential applications in molecular electronics and photonic devices.[1–4] As one of the most promising photochromic molecules, diarylethene molecules have been widely used for data storage and molecular photoswitching because of their short response time, high photoisomerization quantum yield, and outstanding fatigue resistance.[5–8] However, current diarylethene-based responsive systems generally require the use of short-wavelength ultraviolet (UV) or visible light to trigger molecular isomerization, which may cause deleterious effects associated with low-density data storage and the cross-talk between multiple memory layers.[9–13]

Lanthanide-doped upconversion nanoparticles (UCNPs), which can turn near-infrared (NIR) excitation into visible or UV light emission, may provide a much needed solution to the above-mentioned problem.[14–23] Over the past few years, UCNPs and diarylethene-based molecules have been combined for nondestructive optical memory and photoswitching applications.[24–32] Despite the enticing prospect, these demonstrations are constrained by a number of limitations such as complex procedure, slow rates of photoreaction, and the inherent deficiency in data processing due to uncontrolled manipulation of ring-opening and ring-closing reactions of the diarylethene molecules. To this regard, we reason that a dual-channel orthogonal pumping scheme with 980 and 1532 nm lasers, by which the UV and green emissions of lanthanide dopants can be upconverted selectively on a single-particle level, would make rewritable data storage possible. Importantly, in contrast to the previously reported 800/980 nm excitation systems,[13–18] our design provides a precise control over the excitation of different activators, thereby offering the possibility of improving the spectral purity of orthogonal emission. As a result, a reversible photochemical reaction through remote NIR light activation can be readily implemented.

Herein, we demonstrate a facile, two-way photoswitching of DTE molecules (DTE: 1,2-Bis(2,4-dimethyl-5-phenyl-thienyl)3,3,4,4,5,5-hexafluoro-1-cyclopentene) using core–shell structured upconversion nanoparticles that are excitable by both 980 and 1532 nm lasers (Figure 1a). In a typical experiment, multilayer \( \text{NaYF}_4: \text{Er} \oplus \text{NaYF}_4: \text{Tm} \oplus \text{NaYF}_4 \) nanoparticles were first synthesized to allow for dual-channel excitations (Figure 1b). By tuning the shell thickness of the \( \text{NaYF}_4: \text{Yb} \oplus \text{Tm} \) layer, we obtained power-independent orthogonal luminescence (UV emission of \( \text{Tm}^{2+} \) under 980 nm excitation and green emission of \( \text{Er}^{3+} \) under 1532 nm excitation) with a high spectral purity, which was further utilized to enable reversible processing of data recording and erasing.

In our design, a layer-by-layer epitaxial growth procedure was adopted to introduce different activators into specific layers at precisely defined concentrations (Figures S1 and S2 and Scheme S1, Supporting Information). For orthogonal upconversion to proceed in favor of a precisely controlled photoreaction of DTE, \( \text{Er}^{3+} \)
was confined in the core for generating green emission under 1532 nm excitation,\(^{[39–43]}\) while \(\text{Yb}^3^+\) and \(\text{Tm}^3^+\) were codoped into the shell layer to enable UV emission under 980 nm excitation (Figure S3, Supporting Information). To prevent the energy transfer (ET) from \(\text{Yb}^3^+\) to \(\text{Er}^3^+\) and restrain the cross-relaxation of the excitation energy between \(\text{Er}^3^+\) and \(\text{Tm}^3^+\), we further introduced an inert interlayer of \(\text{NaYF}_4\) between the core and \(\text{NaYF}_4: \text{Yb}/\text{Tm}\) shell layer. Similarly, the \(\text{NaYF}_4\) coating at the outermost layer of the nanoparticles was applied in order to eliminate the surface-related quenching of luminescence (Figure 1b).

It is important to note that \(\text{Er}^3^+\) ion has an absorption band around 980 nm (Figure S4, Supporting Information).\(^{[44–47]}\) To attain the proposed orthogonal upconversion, one must cut off the pathway of 980 nm photons to the \(\text{Er}^3^+\) ions doped in the particle’s core. We hypothesized that a heavy doping of \(\text{Yb}^3^+\) ions in \(\text{NaYF}_4: \text{Yb}/\text{Tm}\) shell may prevent the 980 nm photons from reaching \(\text{Er}^3^+\) in the core region because of a strong absorption of \(\text{Yb}^3^+.\)

To validate our hypothesis, we prepared three batches of core–shell nanoparticles with different thicknesses (3.6, 6.0, 8.2 nm) of \(\text{NaYF}_4: \text{Yb}/\text{Tm}\) shell layer (Figure 2a; Figures S5–S7, Supporting Information). Transmission electron microscopy (TEM) of the samples showed a rod-like shape (Figure 2b). The crystalline nature and hexagonal-phased structure of the as-prepared nanoparticles were further confirmed by high-resolution TEM imaging and the corresponding Fourier transform pattern (Figure S8, Supporting Information). Photoluminescence study revealed that on 980 nm excitation the emission of \(\text{Er}^3^+\) doped in the core decreases in intensity with increasing shell thickness of \(\text{NaYF}_4: \text{Yb}/\text{Tm}\) and the corresponding emission color of the particles changes from cyan to blue (Figure 2c; Figure S9, Supporting Information). Notably, a negligible emission peak (<1%) from \(\text{Er}^3^+\) ions around 545 nm was detected when a 8.2 nm layer of \(\text{NaYF}_4: \text{Yb}/\text{Tm}\) was coated onto the \(\text{NaYF}_4: \text{Er}\) nanoparticles (Figure S10, Supporting Information). This can be explained by considering the fact that most of the 980 nm photons for excitation are consumed by \(\text{Yb}^3^+\) absorption in the shell, leading to inadequate excitation of \(\text{Er}^3^+\) ions in the core. Therefore, only \(\text{Tm}^3^+\) emission was observed upon 980 nm excitation. In addition, with the excitation of different pumping power, the upconversion nanoparticles retained their spectral purity and emission color (Figure 2d; Figure S11, Supporting Information). Strikingly, upon switching the excitation wavelength to 1532 nm, the as-synthesized nanoparticles emitted green-yellow color, which can be attributed to the \(\text{Er}^3^+\) emission (Figure 3a, top spectrum; Figure S12, Supporting Information). Taken together, these results illustrate that, in our
In conclusion, our experiments demonstrate that orthogonal upconversion emissions with high spectral purity can be achieved by core–shell crystal engineering, and that they...
allow light-driven molecular editing to be precisely controlled. Notably, we have shown that multilayered NaYF₄ nanoparticles codoped with Er³⁺ and Tm³⁺ activators at different layers are capable of dual-channel orthogonal-upconversion luminescence on a single-particle level upon excitation at 980 and 1532 nm. This attribute enables to activate a DTE molecule-based reversible photochemical reaction, made possible by the introduction of phototransducers for orthogonal UV–vis radiation as well as subsequent energy transfer to the DTE molecules. The ability to selectively pump Er³⁺ or Tm³⁺ by a 1532 or 980 nm laser makes it possible to obtain high purity emission of Er³⁺ or Tm³⁺ for rewritable optical data storage. With the high registry of optical writing and erasing factored in, this approach could also lead to new techniques of manipulating and controlling electronic devices with NIR light.

Experimental Section
The experimental details are provided in the Supporting Information.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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cyclization reaction, high spectral purity, optical memory, orthogonal upconversion, reversible photoswitching

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