Near-Infrared All-Optical Switching Based on Nano/Micro Optical Structures in YVO\(_4\) Matrix: Embedded Plasmonic Nanoparticles and Laser-Written Waveguides

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Nonlinear interactions between light and matter give rise to a wide range of applications for both fundamental and applied research. Herein, near-infrared switching of the optical response based on embedded Ag nanoparticles and laser-written optical waveguides within yttrium vanadate (YVO\(_4\)) crystal matrix is demonstrated. Using broadband transient absorption spectroscopy with a combination of femtosecond Z-scan spectroscopy, the plasmon-enhanced features of the third-order optical nonlinearity in Ag:YVO\(_4\) nanocomposite at the near-infrared band are elucidated. Meanwhile, an optical-lattice-like microscale waveguide is fabricated with well-preserved photoluminescence properties by femtosecond laser writing. Taking advantage of the ultrafast on–off switching behavior of Ag:YVO\(_4\) saturable absorber, a Q-switched pulsed laser operation in the waveguide platform, delivering 1 \(\mu\)m light pulses with high peak power of 298 mW, is demonstrated. This work indicates a possible path for the development of chip-scale ultrafast photonic devices.

1. Introduction

The plasmonic metallic nanoparticles (NPs) have attracted considerable research efforts in the past few decades.\(^1\)–\(^4\) The collective oscillation of free electrons in metallic nanostructures can be strongly coupled to the external optical stimulation, leading to the excitation of localized surface plasmon resonance (LSPR). Inspired by the unique optical properties of NPs, tremendous progress has been made in diverse fields, including subwavelength imaging,\(^5\) high harmonic generation,\(^6\) and chemical sensors,\(^7\) etc. The most commonly used way to fabricate plasmonic NPs is chemical synthesis and electron beam lithography. And the fabricated NPs have shown their potential as optical switches for pulsed lasing,\(^8\)–\(^11\) which is an important complement of 2D material saturable absorbers.\(^12\)–\(^19\) However, the synthesized NPs are typically directly exposed in air, which can be easily degraded or contaminated. Recent developments in the field of ion beam technology have led to a renewed interest in embedded plasmonic NPs that can be encapsulated at various functional substrates.\(^20\) The high degree of flexibility offered by ion beam implantation (e.g., ion species, energy, fluence, and angle) can facilitate the controllable fabrication of embedded NPs with desired sizes, shapes, distribution, and dielectric environment that meet the practical needs of high integration and high stability. The light-driven LSPR effect of embedded NPs can result in strong scattering and absorption of light.\(^21\) Meanwhile, the electromagnetic field and optical nonlinearity can be significantly

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enhanced in the surrounding matrix while maintaining the ultrafast recovery time.[22] Therefore, matrix embedded with NPs offers superior options to serve as ultrastable nonlinear optical modulators in compact laser sources. For example, Au NPs have been used to tailor the nonlinear response of LiNbO$_3$,[23] and Ag NPs have been used to enhance the third-order optical nonlinearity of SiO$_2$ (fused silica) and YAG crystal.[24,25] Yttrium vanadate (YVO$_4$) crystal is a widely used optical component with wide transparency range and large birefringence, as well as an ideal host for solid-state lasers.[26] The successful fabrication of embedded plasmonic NPs and an understanding of its optical properties within these systems will facilitate the future development of integrated photonics circuits. At the same time, waveguide-based pulsed lasing has attracted more and more attention in recent years.[27–33] Femtosecond laser writing has emerged as a powerful tool to fabricate 3D microstructures inside the transparent functional materials.[34–38] With the light confinement within the microstructures, the intracavity light intensity can be greatly enhanced with lower lasing thresholds and enhanced slope efficiencies compared with bulk systems.

In this article, we propose a new design of compact laser source by combing the ion-implanted embedded NPs with the laser-written optical waveguide in a single chip based on the same YVO$_4$ matrix. The composite material exhibits unique and strongly enhanced optical properties in the near-infrared (NIR) arise from the great enhancement of electric fields induced by LSPR. The ultrafast dynamic response of the composite material is investigated with an unprecedented spectral coverage spanning from the visible toward the infrared region (520–1500 nm) using femtosecond transient absorption spectroscopy. Combined with femtosecond Z-scan spectroscopy, pronounced ultrafast saturable absorption has been observed in the NIR region that can be harnessed in pulsed laser operation in a femtosecond laser-written waveguide platform.

2. Results and Discussion

Figure 1a shows the schematic illustration of the sample fabrication (see the Experimental Section for more details). For an intuitive observation of the morphology and distribution, the cross-sectional transmission electronic microscopy (TEM) was conducted, as shown in Figure 1b (See details in the Experimental Section). It is shown that the Ag NPs were successfully fabricated and distributed below the sample surface with a depth of 60 nm. In addition, element mapping was performed based on energy dispersive X-ray spectroscopy (EDXS), confirming the composition of the Ag NPs within the YVO$_4$ matrix (inset of Figure 1b). As shown in Figure 1c, the high-resolution transmission electron microscopy (HRTEM) was also performed to gain further information of Ag NPs. Figure 1d shows the measured selected area electron diffraction (SAED) pattern of the matrix, and the white dot corresponds to (220), (020), and (200) planes with lattice spacings of 0.2453 ± 0.0047 nm, 0.3456 ± 0.0044 nm, and 0.3533 ± 0.0027 nm, respectively. The SAED pattern of the embedded Ag NPs (Figure 1e) confirms the polycrystalline features. The three distinguished colorful marks of the diffraction pattern can be assigned to (110), (200), and (111) planes with lattice spacings of 0.2843 ± 0.0027 nm, 0.2305 ± 0.0015 nm, and 0.2025 ± 0.0015 nm, respectively.

Figure 2a shows the extracted diameter distribution of embedded NPs based on the TEM image, indicating a mean diameter of 4 nm. For further understanding of the ion implantation process in the crystal, we simulated the ion distribution and the stopping powers by the code of Stopping and Range of Ions in Matter (SRIM).[39] Figure 2b shows the simulated penetration depths of energetic Ag$^+$ ions, showing a Gaussian-like density distribution that agrees well with the TEM cross-sectional image. In addition, as shown in Figure 2c, we calculated the electronic stopping power ($S_e$) and nuclear stopping power ($S_n$) as a function of penetration depth beneath the surface. Both $S_e$ and $S_n$ play an

![Figure 1](image1.jpg)

**Figure 1.** a) Experimental schematic of the ion implantation process. b) The cross-sectional TEM micrograph of the embedded Ag NPs fabricated in YVO$_4$ crystal. The inset is the element mapping. c) The HRTEM image of the embedded Ag NPs. d) The SAED pattern of the YVO$_4$ lattice. e) The SAED pattern of the embedded Ag NPs lattice.
essential role in the energy transfer process during ion implantation, accompanied by the deceleration of energetic ions.

The linear optical absorption properties of the embedded Ag sample are investigated by a UV–Vis–NIR spectrophotometer (Cary 5000). As shown in Figure 2d, there is a clear LSPR peak located at 505 nm for the composite material, further confirming the formation of Ag plasmonic NPs. Interestingly, there is a noticeable absorption enhancement of the composite material in the NIR region, which offers its potential to be applied as a saturable absorber in the NIR band. The linear absorption of the Ag:YVO₄ composite can also be simulated according to the Mie theory\(^{[40]}\)

\[
\gamma = \frac{18\pi p_{\epsilon_d}^{3/2}}{\lambda_0} \frac{\epsilon_m''}{\epsilon_m + 2\epsilon_d} \frac{1}{\lambda_0^2}
\]

(1)

\[
\sum a_i\gamma_i = \gamma_{\text{sum}}
\]

(2)

where \(\epsilon_d\) and \(\epsilon_m\) represent the complex dielectric constants of dielectric and metal, respectively. \(p\) represents the volume fraction of metal \((p = 0.1)\), and \(\lambda_0\) is the light wavelength. \(\gamma_i\) and \(a_i\) correspond to the influence factor and absorption of Ag NPs with diameters \(i\), respectively. Figure S1, Supporting Information, shows the simulation results of the absorbance with seven different NP diameters. The simulated LSPR peaks and overall trends are consistent with the observed experimental result. As shown in Figure S2, Supporting Information, the near-field enhancement of Ag:YVO₄ nanocomposite at NIR is simulated by the numerically solving Maxwell’s equations based on the discrete dipole approximation (DDA) method.\(^{[41]}\)

To gain signatures of the origin of absorption enhancement in the infrared range, we real-time investigated the ultrafast optical response of embedded Ag NPs composite in an unprecedented spectral coverage from the visible to the NIR (see the Experimental Section for more details). The pump laser used in this work is 35 fs laser pulses with the photon energy centered at 2.48 eV, driving the electron distribution of this system far from equilibrium on a much shorter timescale than the electron–photon scattering time. The changes of electron distribution after excitation would perturb the real and imaginary parts of the dielectric function and in return modify their optical response. The temporal and spectral evolution of different optical transitions can be monitored by another ultrashort laser beam with well-defined time delays. The ultrafast dynamic response can therefore be real-time recorded with an optical fiber-coupled multichannel spectrometer by measuring the pump-induced differential absorption contrast \(\Delta A\) as follows

\[
\Delta A = \log_{10} \frac{I_0}{I_{\text{pump} + \text{probe}}} - \log_{10} \frac{I_0}{I_{\text{probe}}} = \log_{10} \frac{I_{\text{pump} + \text{probe}}}{I_{\text{pump} + \text{probe}}} \log_{10} \frac{I_{\text{pump} + \text{probe}}}{I_{\text{pump} + \text{probe}}}
\]

(3)

where \(I_0\) is the intensity of the probe beam incident on the sample, and \(I_{\text{pump} + \text{probe}}\) and \(I_{\text{probe}}\) are the intensity of the probe beam transmitted through the sample with or without the pump.
beam, respectively. Meanwhile, all the acquired data are corrected, considering the wavelength-dependent chirp and background scattered light.

As shown on a logarithmic scale in Figure 3a, we obtained the 2D differential absorption contrast as a function of probe laser wavelength and time delay in the visible band for the first 1000 ps. The sample exhibits a distinct transient optical response when probed at different laser wavelengths. As the pump photon energy is much smaller than the transition energy from d band to the Fermi surface (3.7 eV in silver), the interband transition is not considered. The energy of the light pulses can transfer its energy to the electron gas by free-carrier absorption instead of perturbing the d-band electrons. Therefore, we can create a non-Fermi distribution with 2.48 eV energies higher than the Fermi level and mimic the nonequilibrium scenario of this work for intraband excitations. When the probe laser wavelength approaches the plasmonic resonance energy, we observe a pronounced optical bleaching signal that arises from the LSPR effects of metal NPs. Figure 3b shows the temporal evolution of the absorption contrast near the LSPR peak. Following optical driving, the ΔA signal experiences a sharp increase in its intensity with a rise time of 219.4 fs. During the early femtosecond timescale, the electronic system gets thermalized, and the energy is redistributed to a hot Fermi distribution through electron–electron interactions. Meanwhile, a giant enhancement of the near field is expected to occur. For longer timescales, the electron gas would lose its energy and transferred to the silver lattice due to an electron–phonon scattering process, leading to equilibration of the electron and lattice temperature. Finally, the excess energy from the Ag NPs will be transferred to the surrounding matrix on a timescale of hundreds of picoseconds. Interestingly, there is an obvious nonlinear transient optical response when we tuned our vision to the NIR region (Figure 3c,d). Coincidentally, the intensity of the transient signal reaches its maximum at 150 fs, which is comparable with the timescale of LSPR observed in the visible region. Therefore, the observed ultrafast response at the NIR regime can be related to the plasmon resonance-enhanced nonlinear optical processes during the dephasing of light-driven LSPR mode. At the same time, we recorded spectral changes at different times. Figure 4a shows the extracted temporal evolution in the NIR spectral domain. As can be seen, there is an obvious spectrum broadening and redshift in the early times. The spectral shape is much higher and wider because of the great LSPR enhancement of electric fields can induce a variation of electron occupancy in a broad range. The changes of the electron distribution during the electron gas thermalization can modify the intraband electronic transitions and therefore the infrared optical response of the sample. Meanwhile, to obtain the relaxation times at 1 μm (Figure 4b), the kinetics can be well fitted by a biexponential decay function convoluted with a Gaussian instrument response function (IRF) as follows

\[
y(t) = \left[A \left( e^{-\frac{t}{\tau_1}} + e^{-\frac{t}{\tau_2}} \right) \right] \ast e^{\left(\frac{-t}{t_0}\right)} \cdot \frac{IRF}{2 \cdot \ln 2}
\]

where * represents convolution, \( A \) is the amplitude, \( \tau_1 \) is the relaxation time, and \( t_0 \) is time zero. The IRF is measured to be \( \approx 100 \text{ fs} \) with a routine cross-correlation procedure. As shown in Figure 4b, the fast relaxation time \( \tau_1 \) is fitted to be 219.4 ± 23 fs and can be attributed to the rapid intraband relaxation that cools
the carriers down to the band edge. The slow component $\tau_2$ is fitted to be $7.435 \pm 1.27$ ps and represents the electron–phonon scattering process. The standard deviation $\sigma$ can be calculated to be as low as 0.000491 as follows

$$\sigma = \sqrt{\frac{\sum(S_{\text{exp}} - S)^2}{n - 1}}$$

where $S_{\text{exp}}$ is the experimental data of a single point, $S$ is the fitted data, and $n$ is the number of data points.

To gain further knowledge of the nonlinear absorption properties, an open-aperture Z-scan technique is utilized with an infrared femtosecond laser (1030 nm, 340 fs, and 100 Hz) excitation (see the Experimental Section for more details). As shown in Figure 4c, there are negligible nonlinear absorption effects for the pristine YVO$_4$ matrix. In contrast, for Ag:YVO$_4$ nanocomposite, an obvious nonlinear saturable absorption effect is observed as shown in the positive response in the nonlinear transmission during the laser focus ($Z = 0$), which indicates its potential as a Q-switch in the pulsed laser generation. The nonlinear transmission as a function of the excitation densities is also shown in Figure 4d. The nonlinear optical response traces can be fitted by the following equation

$$\alpha(I) = \frac{\alpha_S}{1 + \left(I/I_S\right)} + \alpha_{NS}$$

where $I_S$ is saturation intensity, $\alpha_S$ is modulation depth, and $\alpha_{NS}$ is the nonsaturable component. By fitting the open-aperture Z-scan data, the saturation intensity and modulation depth can therefore be obtained to be 3.2 GW cm$^{-2}$ and 14.2%. Table 1 shows the third-order typical embedded material systems. Notably, the modulation depth in this work is much higher than previous embedded systems (e.g., 1.1% of Ag:SiO$_2$ and 2.7% of Ag:YAG) at the same wavelength, which indicates that Ag:YVO$_4$ sample can be used as a promising new nonlinear absorption material for light modulation. Overall, the observed ultrafast relaxation and superior saturable absorption response (e.g., high modulation depth and low saturation intensity) endow Ag:YVO$_4$ with a great potential for modulating the intracavity losses toward all-optical switching applications.

![Figure 4.](image_url)

**Figure 4.** a) Differential absorption spectra obtained with time delays between 0.1 and 140 ps at room temperature. b) Transient optical response probed at 1064 nm. c) Normalized transmission as a function of sample position $Z$. d) Plot of transmission as a function of input intensity of the femtosecond laser.

**Table 1.** Third-Order nonlinear properties of embedded NPs.

| Embedded NPs | Matrix   | Wavelength [nm] | Saturation intensity [GW cm$^{-2}$] | Modulation depth [%] | Reference |
|--------------|----------|----------------|-----------------------------------|----------------------|-----------|
| Au           | LiNbO$_3$| 1030           | 98.14                             | –                    | [23]      |
| Ag           | SiO$_2$  | 1030           | –                                 | 1.1                  | [24]      |
| Ag           | YAG      | 1030           | 0.63                              | 2.7                  | [25]      |
| Cu           | LiTaO$_3$| 1030           | 3.77                              | 1.8                  | [44]      |
| Ag           | YVO$_4$  | 1030           | 3.2                               | 14.2                 | This work |
To verify the potential of Ag:YVO$_4$ as an all-optical modulator, we propose a compact laser device based on micro/nano mixed structure combining fabricated embedded NPs with monolithic waveguide in the same YVO$_4$ matrix (Figure 5a). To fabricate the light-guiding microstructures, we use a femtosecond laser to interact with the Nd:YVO$_4$ crystal, forming a new design of optical waveguide with optical-lattice-like structure as shown in the inset of Figure 5a (See details in the Experimental Section). The high energy femtosecond laser pulses can interact with YVO$_4$ matrix through nonlinear absorption processes (e.g., multiphoton ionization and avalanche ionization), leading to the defect formation and permanent localized decrease in the refractive index near the laser focus without fast heat transfer process. Therefore, the waveguide can be fabricated with the desired circular shape surrounded by low refractive index tracks. As shown in Figure 5b and Figure S3, Supporting Information, the photoluminescence of the waveguide core is well preserved compared with the unmodified bulk region. The inset is the microphotoluminescence mapping of the whole waveguide structure which is related to the NIR transitions of $^4F_{3/2} \rightarrow ^4I_{11/2}$ (Figure 5b) and $^4F_{3/2} \rightarrow ^4I_{9/2}$ (Figure S3, Supporting Information). For the laser generation in a waveguide platform, we use a typical end face coupling arrangement (See details in the Experimental Section). The pump light is centered at 808 nm and can be efficiently coupled into the waveguide. Based on the laser configuration, we have achieved a stable pulsed waveguide laser operation at 1 $\mu$m. Figure 3 shows the emission spectrum of the waveguide laser, showing a clear peak at a central wavelength of 1064 nm. The recorded oscilloscope traces are shown in Figure 5c and Figure S4, Supporting Information, showing Q-switched pulses generated with our micro/nano mixed structure are quite stable. Figure 5e shows measured average output power as a function of launched power by linear fitting. The maximum output is 85 mW and the slope efficiency reaches 20%. The switching parameters can be adjusted by changing the launched power. Figure 5f shows the relationship between repetition rate and pulse duration as a function of launched power. Figure 5g shows pulse energy and peak power as a function of launched power.

Figure 5. a) Prototype and spatial configuration of femtosecond laser writing of optical-lattice-like cladding waveguide and the compact laser design modulated by embedded Ag NPs. The inset is the optical micrograph of the fabricated waveguide. The white scale bar is 20 $\mu$m. b) Microphotoluminescence obtained from the waveguide core and the unmodified track. The inset is the intensity microphotoluminescence mapping of the whole microstructure related to the NIR transition of $^4F_{3/2} \rightarrow ^4I_{11/2}$. c) The emission spectrum of the output waveguide laser with a central wavelength of 1064 nm. d) The recorded pulse trains show an all-optical switching of the optical intensity based on Ag:YVO$_4$ modulator. e) The average output power as a function of the launched power. f) Repetition rate and pulse duration as a function of launched power. g) Pulse energy and peak power as a function of launched power.
rate (pulse duration) is tunable, ranging from 4.13 MHz (38 ns) to 13.3 MHz (21 ns), respectively. The dependence of pulse energy and peak power is shown in Figure 5g, and the maximum pulse energy and peak power of a single pulse can reach 6.27 nJ and 298 mW. Most of the previous works only achieved a mixed state of Q-switched and mode-locking, which is typically considered as not stable. The high modulation depth and low saturation intensity of Ag:YVO₄ endow the realization of all-optical switching functionalities instead of the insufficient mixed state of Q-switched mode-locking operation in an optical waveguide.

3. Conclusion

In summary, embedded silver NPs are successfully fabricated within YVO₄ matrix and their ultrafast optical properties are investigated by broadband transient absorption spectroscopy and femtosecond Z-scan spectroscopy. Based on the superior ultrafast nonlinear absorption properties, we demonstrate ultrafast all-optical switching in the NIR region, which features femtosecond response speed as well as pronounced saturable absorption. Furthermore, a novel laser design is constructed by combing the laser-written optical-lattice-like Nd:YVO₄ waveguides and embedded NPs as a Q-switch. Our work demonstrates the potential applications of plasmon-based micro/nano structures for high performance all-optical signal-processing devices in integrated optics.

4. Experimental Section

**Embedded NP Synthesis:** During the experiments, the energetic Ag⁺ ions (100 keV) were implanted into an optically polished YVO₄ matrix (10 × 10 × 2 mm³) at a fluence of 1 × 10¹⁷ ions cm⁻² using an ion-implanter LC22-1CD-01 at Wuhan University. The randomly distributed encapsulated ions would aggregate and form the embedded NPs when the concentration was over the solubility limit, while without the extra assistant of heat treatment.

**Morphology Characterization:** The sample was first bonded by M-bond 610 and grinded to a cross-sectional TEM specimen. During TEM sample preparation, a Gatan 691 type Ion Beam Thinner was used with the voltage (angle) gradually decreased from 4.8 kV (10⁸) to 3 kV (4°). The morphologies and crystallographic information were then obtained using a Tecnai G2 F20 S-TWIN (FEI) operated at 200 kV with a 0.24 nm point resolution, a 0.102 line resolution, and a 0.14 information resolution.

**Linear Optical Characterization:** The linear optical response of the sample was measured by using a UV–vis–NIR spectrophotometer (Agilent, Cary 5000), covering a wide spectral range from 300 nm to 1500 nm. The light source switching wavelength was 350 nm, the detector switching wavelength was 800 nm, the scanning data interval was 0.5 nm, the average time was 0.1 s, and the scanning speed was 300 nm min⁻¹.

**Femtosecond Transient Absorption Spectroscopy:** The broadband transient absorption spectroscopy utilized a Ti:sapphire ultrafast amplifier (Coherent, MBR-PE). The pump wavelength was tunable to achieve the best efficiency. The generated pump pulses were then coupled into the waveguide using a convex lens with a 25 mm focal length. A set of laser mirrors were used to construct a waveguide resonant cavity. The output laser was collected with a 20× microscope objective lens after passing through a long-pass filter (Thorlabs, FEL0850). The filtered free-space laser was then coupled to a single-mode fiber that was connected with a high-speed fiber optic InGaAs photodetector (New focus, 1414 model) and a real-time digital oscilloscope (Tektronix, MSO 72504DX).

**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.

**Keywords**

integrated photonic devices, ion implantation, localized surface plasmon resonance, nonlinear optical materials, plasmonic nanoparticles
