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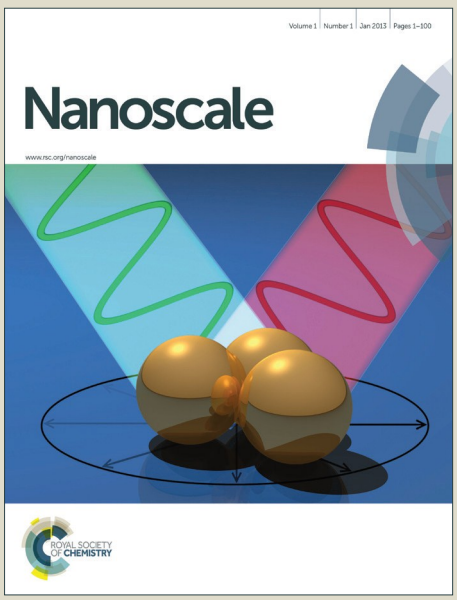

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Plasmonic random laser tunable through stretching silver nanowires embedded in a flexible substrate

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Abstract

A mechanically-tunable random laser based on a waveguide-plasmonic scheme is investigated. This laser can be constructed by spin coating of a solution of polydimethylsiloxane doped with rhodamine 6G organic dye and silver nanowires onto a silicone rubber slab. The excellent overlap of the plasmon resonance peak of the silver nanowires with both the pump wavelength and the photoluminescence spectrum provides the low threshold and tuning properties of the random laser. The random laser wavelength can be tuned from 558 to 565 nm by stretching the soft substrate, which causes reorientation and break of the silver nanowires. The polarization state of the random laser can also be changed from random polarization to partial polarization by stretching. The laser performance remains unchanged after the stretching and restoration experiments. These results not only enable easy realization of an ultrathin flexible plasmonic random laser but also provide insights into the mechanisms of three-dimensional plasmonic feedback random lasers.

KEYWORKS: Tunable random laser, plasmonic feedback, soft matters.

Random lasers have attracted widespread attention because of their unique optical properties and potential applications[1–6]. In particular, random lasers based on plasmonic scattering or plasmonic feedback provided by metallic nanostructures have been reported in both solutions and thin films by a number of researchers[7–12]. Solid-state plasmonic random lasers offer low thresholds because of their good optical confinement and strong plasmonic enhancement properties[7,13]. However, the flexibility and tunability of random lasers have caused researchers some concern. Non-tunable random lasers have been successfully constructed on soft substrates to demonstrate their mechanical flexibility[14,15]. Wiersma *et al.* reported on their observations of a temperature-tunable random laser in sintered glass with fascinating emission properties[16]. Correspondingly, both flexibility and tunability urgently need to be achieved simultaneously in plasmonic random lasers.

Recently, we demonstrated a plasmonic feedback random laser that consisted of randomly distributed gold nanoisland structures covered by a dye-doped polymer film[7]. In this paper, we take advantage of the natural flexibility of silicone rubber slabs and polydimethylsiloxane (PDMS) to alter the distribution and orientation of the silver (Ag) nanowires contained therein, which in turn tunes the plasmon resonance wavelength at which strong plasmonic feedback is obtained. The robustness of the tunable plasmonic random laser's performance is ensured by stretching and restoring experiments. The results reported here offer a simple and straightforward method to mechanically tune the emissions of plasmonic random lasers.

The uniform bicrystalline Ag nanowires were synthesized by a soft solution-phase approach[17], and were then dispersed in an ethanol solution of rhodamine 6G (R6G) to obtain Ag nanowire ink with a 0.033-M concentration. The R6G concentration is 3 mg/mL. The Ag nanowire ink and PDMS were then mixed at a volume ratio of 1:5 in

an ultrasonic tank (250 W, 40 kHz) for 10 min. The blend solution was spin-coated onto a silicone rubber slab with an area of 20 mm×20 mm and thickness of 1 mm at a speed of 1000 rpm, forming a thin film with thickness of approximately 50 μm. The PDMS preparation process is similar to the process described in our recent work[18]. The sample was placed on a hot plate at 80°C for 30 min to complete the cross-linking polymerization and drying processes. After cooling to room temperature, a flexible plasmonic random laser device was realized, as shown in Fig. 1 (a).

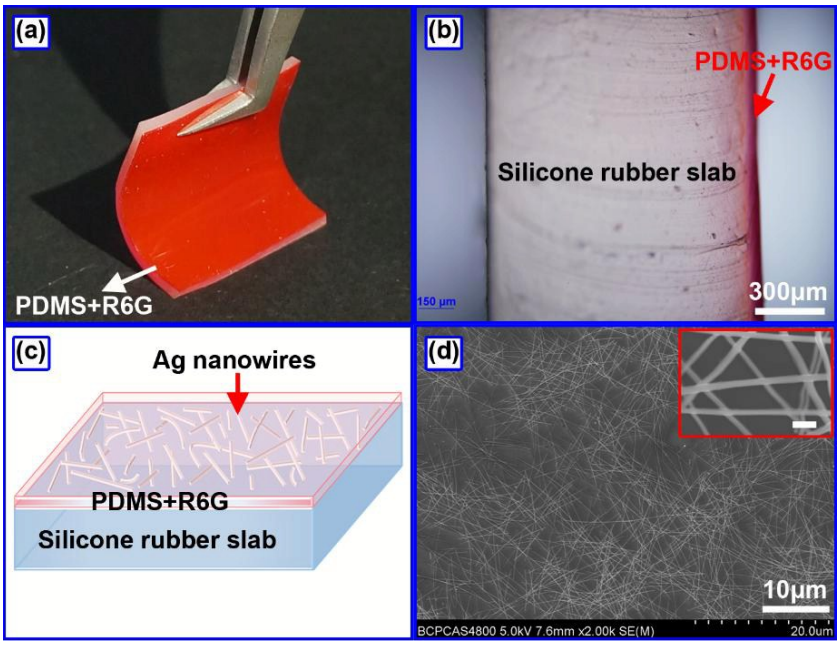

Figure 1. (a) Photograph of the random laser sample. (b) Optical micrograph of the side view of the sample. (c) Schematic of a flexible plasmonic random laser. (d) SEM images of the Ag nanowires. The inset shows an enlarged view of the nanowire cluster. The scale bar in the inset represents 200 nm.

Figure 1(a) and (b) shows a close-up view and a side view of the random laser sample, respectively. The PDMS film thickness is sufficiently uniform to enable it to act as a waveguiding plasmonic gain channel as shown in Fig. 1(c). Ag nanowires embedded in the PDMS films form a three-dimensional (3D) network structure. Figure 1(d) shows scanning electron microscopy (SEM) images of the Ag nanowire cluster. A few drops of the Ag nanowire ink with 0.033-M concentration were placed on top of a glass

substrate and were then dried naturally. The mean diameter and the mean length of the Ag nanowires are 70 nm and 10 μm, respectively. The nanowire cluster morphology shown in Fig. 1(d) is very similar to that of the nanowires in the PDMS film, and this will be discussed later in the paper.

The PDMS film doped with the Ag nanowires and R6G forms a waveguiding plasmonic gain channel. The dye radiation is significantly enhanced via excitation of the localized plasmon resonance of the nanowires as shown in Fig. 2(a). This enhancement can be ascribed to the overlapping of the localized plasmon resonance of the Ag nanowires with both the emission spectrum of the dye molecules and the pump wavelength. The R6G-doped PDMS film acts as an active waveguide layer to provide the plasmonic feedback mechanism, which is very similar to the observations of our previous work[7]. The overlap between the plasmon resonance spectrum and the pump wavelength enables strong pump light scattering inside the waveguide, which will in turn improve the pump efficiency of the random laser. In addition, the system presented here can provide 3D plasmonic feedback because of the metal nanostructures distributed within the active layer. Most of the scattered light is confined within the active waveguide layer and is then scattered by the Ag nanowires embedded in the waveguide, which leads to high efficiency amplification.

In the experiment, a frequency-doubled neodymium-doped yttrium aluminum garnet (Nd:YAG) pulsed laser with a wavelength of 532 nm is used as the pump source for the random laser, which then produces 30-ns laser pulses at a repetition rate of 10 Hz and with pulse energies of up to 50 mJ. Laser pulses with a radius of approximately 5 mm were irradiated on the PDMS film at an angle of incidence of 30º. Figure 2(a) shows that the plasmon resonance peak of the Ag nanowires overlaps with both the pump wavelength and the photoluminescence spectrum of R6G, which supports the formation

of plasmonic gain channel. The electric field distribution of the Ag nanowire is calculated at the excitation wavelength of 532-565 nm with a step of 1 nm. Strong local field enhancement can be observed at all wavelengths. A typical electric field distribution is shown in Fig. 2(b). The simulations were done using the finite element method with the commercially available software package COMSOL. The permittivity of Ag is chosen from Johnson and Christy's experimental data[19]. The diameter and the length of the Ag nanowire are 70 nm and 1 μm, respectively. Figure 2(c) shows the spectra of the random laser emissions at various pump power densities, which were measured using a spectrometer (Ocean Optics Maya 2000 Pro). The random laser emission is centered at approximately 565 nm, with a full width at half maximum (FWHM) of about 5 nm. The intensity and the FWHM of the output laser are shown as functions of the pump power density in Fig. 2(d), which indicates a pump threshold of approximately 0.31 MW/cm^2, as indicated by the black arrow.

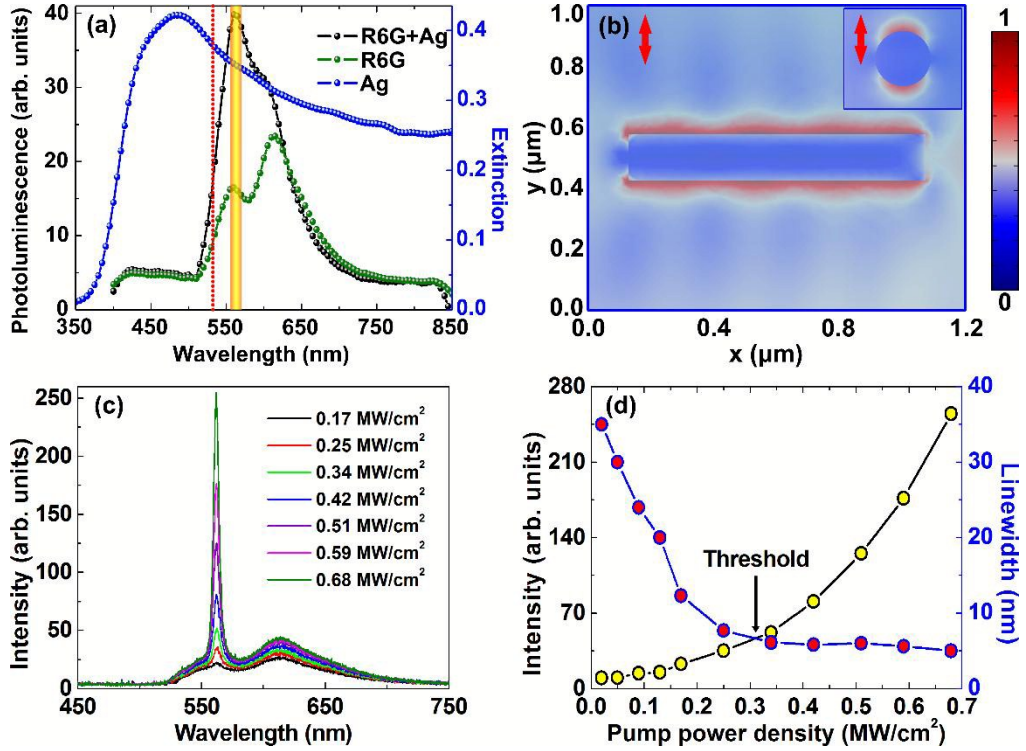

Figure 2. (a) The extinction and the photoluminescence spectra of Ag nanowires and R6G doped

in PDMS. The red dotted line and the yellow shaded area indicate the pump and the emission wavelengths, respectively. (b) The electric field distribution of the Ag nanowire at the excitation wavelength of 560 nm. The red arrows denote the polarization of the excitation beam. The inset is a cross-sectional view. (c) Spectra of the random laser emissions at various pump power densities. (d) The intensity and FWHM of the output laser as a function of pump power density, which indicate a pump threshold of about 0.31 MW/cm^2.

The PDMS film with embedded Ag nanowires forms the waveguiding plasmonic feedback mechanism and supports the random lasing action of the dye. Thus, the spectral position of the random lasing process can be tuned by simply stretching the PDMS film. Two opposing edges of the sample are clamped to two separate translation stages to allow the translation of the stages to stretch the sample quantitatively. Microscopic images of the Ag nanowires embedded in the PDMS film are shown in Fig. 3 (a) and (b). Stretching of the PDMS film induces microscopically inhomogeneous deformations inside PDMS film, which play a key role in the reorientation and fracture of Ag nanowires in PDMS. The size of the deformations is in the range from microns to hundred microns[20]. The random orientations of the Ag nanowires in Fig. 3(a) will align in parallel with the stretching direction as shown in Fig. 3(b). The long nanowires are likely to break into shorter pieces about 10 μm under tensile force, as shown in the inset in Fig. 3(b), which makes the Ag nanowire length distribution more uniform. Most of the nanowires remain intact in Fig. 3(b). The stretching amount can be approximately estimated by the "duty ratio" of the fractured Ag nanowire. The ratio between the total gap widths and the length of fractured nanowires is around 30% as shown in the inset in Fig. 3(b). The orientation distributions of Ag nanowires embedded in the PDMS film before and after stretching were analysed statistically by processing the images in Fig. 3(a) and (b), respectively. The histograms in Fig. 3(c) and (d) show the reorientation of the Ag nanowires controlled by stretching.

The reoriented nanowires will return to the original state when the tensile force is released, guaranteeing the reversibility of the sample. The changes in the distribution and orientations of the Ag nanowires have a considerable influence on the plasmon resonance spectra in Fig. 3(e) and (f).

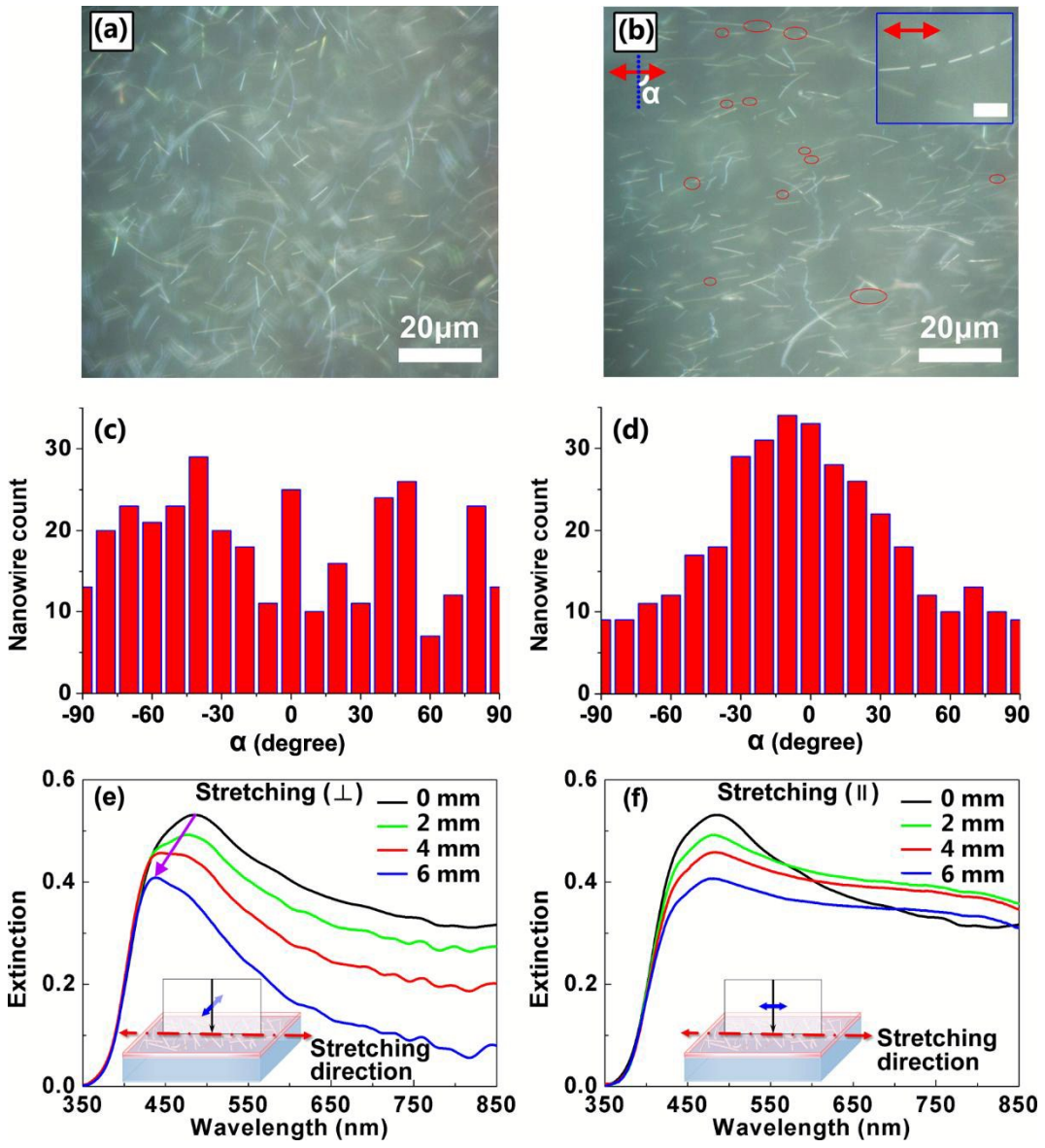

Figure 3. Microscopic images of Ag nanowires embedded in the PDMS film (a) before and (b) after stretching. The red arrows indicate the stretching direction. The broken nanowires are indicated by red circles. The inset in (b) shows that the longer nanowires break into short pieces after stretching. The scale bar in the inset represents 10 μm. (c) and (d) The histograms of the orientation distributions of Ag nanowires over the entire image in (a) and (b), respectively. α is

the angle between the major axis of the nanowire and the stretching direction as shown in (b). (e) and (f) Extinction spectra of the Ag nanowires. The stretching directions are (e) perpendicular to and (f) parallel to the polarization directions of the incident light, which are indicated by the blue arrows shown in the insets. The purple arrow in (e) indicates the blue shift of the spectra.

In the optical extinction measurements, non-polarized light from a tungsten halogen lamp (HL-2000) is used as the white light source. A polarizer is used to alter the polarization direction of the incident white light. Figure 3(e) and (f) shows the extinction spectra of the Ag nanowires for two orthogonal polarization directions. The amplitudes of the extinction spectra decrease with increasing stretching amount because there is less scattering from the Ag nanowires in thinner films. A blue shift and a narrowing of the extinction spectra can be observed when the pump light polarization direction is perpendicular to the stretching direction. This behavior can be ascribed to the uniform length distribution and the reorientation of the Ag nanowires after stretching. A small number of long nanowires break into shorter pieces makes the length distribution more uniform. It is one of the reasons that the plasmon resonance spectra narrows, which is an irreversible process. The reorientation of Ag nanowires is the major reason for the blue shift and narrowing of the extinction spectra, which is a reversible process. Thus, the behavior of the spectral response almost remains unchanged after the stretching and restoration experiments. For the stretching amount of 30%, the peak of the extinction spectrum shifts from about 486 nm to 438 nm, and the FWHM of the spectrum changes from 160 nm to 146 nm. The plasmonic resonance can thus be tuned conveniently by controlling the amount of mechanical stretching. As a result, the random lasing spectra shift correspondingly, as shown in Fig. 4(a). This not only confirms the tunability of the flexible random laser based on the mechanical stretching method but also confirms the 3D plasmonic feedback mechanism for the thin

film waveguide. There is no obvious change in the peak position of the extinction spectra for the parallel case in Fig. 3(f), which implies that the dominant polarization direction of the random laser is perpendicular to the stretching direction. This has been confirmed by our experiments in Fig. 4(b).

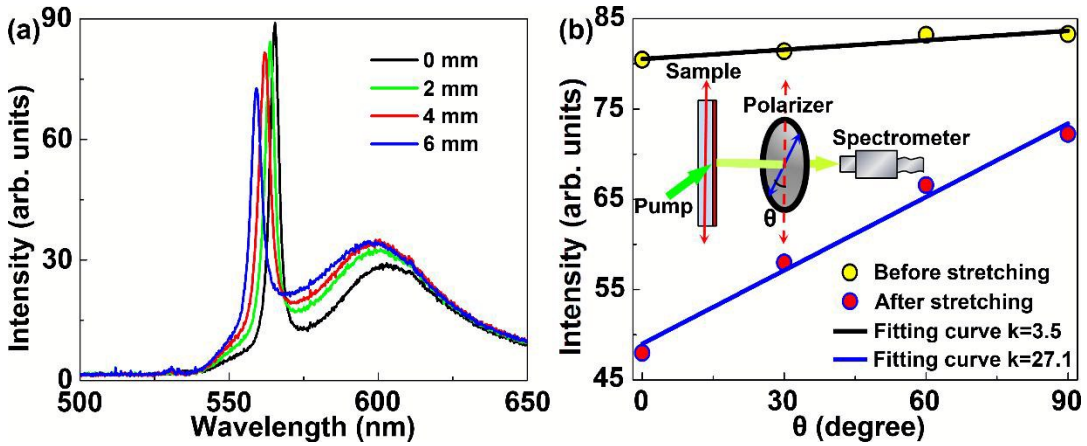

Figure 4. (a) Emission wavelength tuning by stretching the plasmonic random laser device. The emission wavelength shifts from 565 nm to 558 nm when the amount of stretching increases from 0 mm to 6 mm. (b) Polarization state of the random laser before and after stretching. The inset shows the measuring setup. θ is the angle between the polarization direction of the polarizer (denoted by the blue arrow) and the stretching direction (denoted by red arrows).

Figure 4(a) shows the spectroscopic response of the flexible plasmonic random laser device to different amounts of stretching. A blue shift in the emission wavelength can be clearly observed by increasing the amount of stretching with steps of 2 mm. The total stretching amount is 6 mm, which is 30% of the original sample length. The emission wavelength changes from 565 nm to 558 nm when the random laser device is stretched from 0 mm to 6 mm. The tuning range remains basically unchanged when the stretching direction changes from parallel to perpendicular to the pump polarization direction. The amplitude of the emission spectrum decreases with increasing stretching amounts because of weakening of the plasmonic response strength and the broken

feedback loop. This behavior can be understood by referring to the micrographs and the extinction spectra of the sample shown in Fig. 3.

The polarization state of the random laser is measured carefully before and after stretching as shown in Fig. 4(b). A piece of polarizer is placed between the laser sample and the spectrometer probe. The angle θ between the polarization direction of the polarizer (denoted by the blue arrow in the inset in Fig. 4(b)) and the stretching direction (denoted by red arrows in the inset in Fig. 4(b)) changes from 0^o to 90^o with a step of 30^o to measuring the polarization state of the laser. The polarization ratio between parallel ($\theta=0^o$) and perpendicular polarization ($\theta=90^o$) changes from 1.04 (the black fitting curve with a slope of 3.5) to 1.51 (the blue fitting curve with a slope of 27.1). After stretching, the polarization state of the random laser changes from random polarization to partial polarization due to reorientation and break of the Ag nanowires after stretching.

In conclusion, we fabricated a wavelength-tunable random laser based on a waveguiding plasmonic gain channel. The emission wavelength can be tuned from 558 to 565 nm by stretching the flexible laser. The tunability originates from the blue shift and narrowing of the plasmon resonance of Ag nanowires, which is determined by the reorientation and uniform length distribution of Ag nanowires after stretching. The stretching can further affect the polarization state of the output random laser. This technique can be used to design tunable plasmonic devices.

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