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Plasmon-enhanced random lasing in bio-compatible networks of cellulose nanofibers

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We report on plasmon-enhanced random lasing in bio-compatible light emitting Hydroxypropyl Cellulose (HPC) nanofiber networks doped with gold nanoparticles. HPC nanofibers with a diameter of 260 ± 30 nm were synthesized by a one step, cost-effective and facile electrospinning technique from a solution-containing Rhodamine 6G and Au nanoparticles. Nanoparticles of controlled diameters from 10 nm to 80 nm were dispersed inside the nanofibers and optically characterized using photoluminescence, dark-field spectroscopy, and coherent backscattering measurements. Plasmon-enhanced random lasing was demonstrated with a lower threshold than that in dye-doped identical HPC networks without Au nanoparticles. These findings provide an effective approach for plasmon-enhanced random lasers based on a bio-compatible host matrix that is particularly attractive for biophotonic applications such as fluorescence sensing, optical tagging, and detection. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4939263]

In recent years, fiber-based photonic nanostructures made of organic and inorganic materials have attracted an increasing attention due to a number of potential applications to light generation, confinement, guiding, and detection. $^{1-5}$ Among various active nanostructures, polymer-based nanofibers are particularly interesting due to their mechanical strength, flexibility, and bio-compatibility in combination with cost-effective synthesis techniques that do not require hazardous chemicals.^{6,7} High-quality nanofibers can be obtained from solution-based processing using materials composed of cellulose, which is the most abundant biopolymer on Earth and is widely used to produce paper.⁸ In particular, light-emitting thick films made of random networks of cellulose-based nanofibers doped with Au nanoparticles (NPs) can be fabricated from a Hydroxypropyl Cellulose (HPC) aqueous solution by the facile and environmentally friendly electrospinning technique.9,10 The plasmonenhanced scattering properties of such systems combined with their three-dimensional random morphology provide unique opportunities to engineer multiple light scattering and random lasing using biodegradable media.^{11–13}

Random lasers rely on coherent multiple scattering of light in a random medium and have attracted a great deal of research efforts in the last decades.^{14–19} A typical random laser is composed of dielectric material with refractive index fluctuations on the scale of the optical wavelength. Recently, the incorporation of sub-wavelength metallic nanoparticles in dielectric random lasers has been shown to significantly

improve the lasing performances and to decrease the threshold due to enhanced plasmon scattering.^{20–23} Compared to dielectric scatterers, metallic particles display plasmon enhanced optical cross sections and spectrally tunable scattering properties that can be controlled by their shapes and sizes.²⁴ It has also been recently demonstrated that metal NPs can significantly enhance the spontaneous emission rate in a gain medium and increase its performances.²⁵ Although random lasers have been developed from a large class of materials such as semiconductor nanoparticles,¹⁶ polydispersed liquid crystals,²⁶ polymer thin film,²⁷ liquid crystal films,²⁸ and suspensions of dielectric particles in laser dyes,²⁹ random lasing in a random network of nanofibers doped with plasmonic nanoparticles has not been demonstrated yet.

In this paper, we demonstrate plasmon-enhanced random lasing in nanocomposites of highly interconnected random nanofiber networks. These systems are obtained directly from a light emitting HPC water-based solution that contains Au nanoparticles in a Rhodamine 6G (RHG) gain medium. We fabricated thick films with variable thicknesses $(20 \,\mu\text{m}-160 \,\mu\text{m})$ composed of HPC nanofibers with an average diameter of ~ 260 nm. The optical properties of samples with different diameters of Au nanoparticles in the range of 10 nm-80 nm were optically characterized using photoluminescence, dark-field spectroscopy, and coherent backscattering (CBS) measurements. The random lasing properties were demonstrated by pumping the samples with a ps laser (532 nm, 30 ps) at room temperature. Above a pumpthreshold fluence of 4 mJ/cm², lasing peaks appeared in the emission spectrum as a result of coherent amplification in

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the random fiber network. Our results demonstrate that samples doped with Au nanoparticles featuring a plasmon resonance overlapping with the RHG emission result in a significant reduction of the random lasing threshold when compared to active samples without Au nanoparticles.

The RHG doped polymer solution was prepared by dissolving HPC in Deionized water water mixing with RHG dyes followed by stirring for 30 min. The as-prepared solution was kept at room temperature for 4 days in order to achieve a homogeneous solution. The concentration of the final mixture was controlled at 45 wt. % HPC with 0.8 mg/ml RHG. The plasmonic NPs and RHG co-doped polymer precursor were prepared by further adding concentrated Au NPs synthesized by the seeded growth method.³⁰ In Figure 1(a), we show several HPC solutions mixed with RHG dyes and Au NPs of different sizes (10 nm/40 nm/80 nm). The diameters of Au NPs were measured by the dynamic light scattering (DLS) technique (Malvern Instrument) and Transmission Electron Microscope (TEM) analysis. The color of the final solution is changed from orange to red after mixing with Au NPs and becomes darker with increasing size of the Au particles due to the enhanced absorption in the visible range. To create active nanofibers by electrospinning, the HPC mixture was poured into a 10 ml syringe (diameter 18.94 mm). The electrospinning syringe was then mounted to an infusion syringe pump (Braintree scientific) with a 20 gauge needle connected to the positive terminal of a high power voltage source (Gamma high voltage). The precursor (45% HPC) was squeezed out from the needle with 0.4 ml/h flow rate driven by the syringe pump. A 20 kV voltage was applied between the needle and metal plate, and the humidity was controlled as 55%. The polymer precursor ejected from the nozzle and then formed nanofibers after solvent evaporation. The charged HPC nanofibers were neutralized at the collector (kept 20 cm from the needle).



FIG. 1. (a) Au Nps (10/40/80 nm) and RHG doped HPC precursor. (b) SEM and TEM images of RHG doped HPC nanofibers. Insets are the TEM image and digit photo of sample. (c) Photoluminescence spectrum of RHG doped nanofibers and undoped fibers. Insets are bright field image and fluorescence image of RHG doped HPC nanofibers. (d) Dark field scattering spectrum of Au NPs and RHG co-doped HPC nanofibers. Inset is the $\Delta\theta$ of RHG nanofibers doped with different sizes of Au NPs.

The morphology of electrospinning nanofibers observed by scan electron microscopy (SEM) is shown in Figure 1(b). The average diameter of nanofibers is around 260 nm with a standard deviation of 30 nm. The high-resolution TEM image in the inset of Figure 1(b) shows that Au nanoparticles are incorporated uniformly within the nanofibers without evident aggregation. The density of Au NPs in the precursor solution is around $\sim 10^{13}$ cm⁻³ for all the Au NPs doped samples. The photoluminescence spectra of RHG doped HPC nanofibers and undoped samples are shown in Figure 1(c), respectively. The emission peak around 553 nm corresponds to the RHG gain medium inside the HPC nanofibers. A fluorescence image of a representative RHG doped sample, shown in the inset of Figure 1(c), reveals that the RHG dye material is homogeneously distributed within the nanofiber networks. The emission was excited using a mercury lamp in combination with a 510 nm band-pass filter with 10 nm bandwidth for excitation and a 563 nm bandpass with 9 nm bandwidth for emission. Dichroic (462/ 523 nm) beamsplitter was placed in the microscope along with a filter for the excited light.

In order to demonstrate plasmon enhanced random lasing, we characterized the scattering properties of three samples containing Au nanoparticles of different sizes of (10 nm/40 nm/80 nm) using dark-field scattering microscopy in a standard setup with a 100 W tungsten halogen lamp.¹⁰ The scattering spectra in Figure 1(d) show a clear resonance peak that shifts from 550 nm to 676 nm when doping with Au nanoparticles of increasing diameter from 10 nm to 80 nm. These resonant peaks well correspond to the excitation of localized surface plasmons of Au NPs embedded in a HPC dielectric.³¹ CBS measurements³² at 532 nm were performed to investigate the multiple scattering of light and to quantify the transport mean free path of HPC nanofibers (Figure 2(a)). For non-absorbing samples of large thickness, the angular width of the enhanced backscattering cone $\Delta\theta \sim 1/k\ell$, where $k = 2\pi / \lambda$, λ is the wavelength, and ℓ is the transport mean free path. We measured a transport mean free path of 6.78 μ m in purely HPC random networks (i.e., no Au NPs and RHG molecules). With Au NPs and RHG doped in the HPC random networks, the enhanced backscattering cone was broadened due to enhanced scattering and absorption (inset of Fig. 2(b)). It is difficult to determine simultaneously the transport mean free path and the absorption length from the backscattering data. Nevertheless, a notable broadening of the backscattering cone with little reduction of the cone height indicates that the broadening is predominantly caused by enhanced scattering instead of absorption. The monotonic increase of the backscattering cone width with the Au NP size suggests that the scattering strength is increased in HPC samples with larger Au NPs.

In addition to multiple light scattering due to Au NPs, our HPC samples have been shown to display remarkable waveguiding properties¹⁰ at the emission wavelength. Such a behavior contributes to further enhance light-matter coupling through a better field confinement. The waveguiding properties are simply demonstrated by exciting a single nanofiber on a small central area (approximately equal to $4 \mu m^2$) using a focused Ar ion laser at 488 nm (Spectra Physics, 177–602) and imaging the signal at the emission wavelength. As



FIG. 2. (a) Black squares represent the measured backscattered intensity of the cellulose nanofiber film as a function of backscattering angle θ . The intensity at large angle is normalized to 1. Red dashed curve is a theoretical fit with the transport mean free path of 6.78 μ m. Inset: SEM image of the thick nanofiber film used for the backscattering experiment. Film thickness is ~160 μ m. (b) $\Delta\theta$ is the angular width of the backscattering cone in the cellulose nanofiber film doped with dye RHG and Au NPs. The inset shows two backscattering cones from the sample with only RHG (solid line) and that with both RHG and 80 nm Au NPs (dashed line). With the addition of Au NPs, the backscattering cone is broadening with little change in the cone height, indicating that the broadening is predominantly caused by enhanced scattering instead of absorption.

shown in Fig S1 in the supplementary material,³³ we have observed the propagation of the fluorescence all along the selected fiber length including the bend region.

In order to demonstrate random lasing, the samples were optically excited with the second harmonic of a pulsed Nd:YAG laser ($\lambda = 532 \text{ nm}, \tau = 30 \text{ ps}, f_{rep} = 10 \text{ Hz}$). The pump beam was incident at 45° , with respect to the sample surface, see Fig. 3(a). The pump spot diameter could be adjusted between 20 μ m and 400 μ m by shifting the focusing lens (f = 200 mm) along the optical axis. Emitted light from the sample was collected with an aspheric lens (f = 11 mm, NA = 0.25) and refocused onto the entrance slit of a gratingspectrometer ($\Delta\lambda < 0.1$ nm). Upon weak laser excitation, the nanofiber films emitted fluorescence, as shown in Figure 3(b) (red curve). Once the pump fluence was increased to around 4 mJ/cm², narrow peaks appeared in the emission spectrum (Fig. 3(a), blue curve), and they grew superlinearly with pump level, marking the onset for random lasing. When the pump area was small (diameter = $20 \,\mu m$), the emission spectrum was dominated by approximately five to ten individual lasing peaks that were well separated and reproducible over >100 pump shots (see supplementary material³³). These lines correspond to the lasing of optical resonances, formed by disorder-induced scattering, within the nanofiber material. At stronger excitation (>1.5 times threshold fluence) or with a larger pump spot (d > 50 μ m), more lasing lines appeared and merged into a continuous band, reaching a regime of highly multimode lasing.



FIG. 3. (a) Schematic for random lasing experiment setup. The pump light (wavelength = 532 nm, pulse duration = 30 ps) was focused onto the sample with a lens (focal length = 200 nm). Emitted light was collected with an aspheric lens (f = 11 nm, NA = 0.25) and imaged onto the entrance slit of a grating-spectrometer. The pump beam spot was scanned across the sample following the pattern shown in the inset, to characterize the lasing threshold. (b) Measured emission spectra at two pump levels. The red curve shows the smooth fluorescence spectrum of the laser-dye below the lasing threshold. The blue curve shows the lasing peaks above the threshold. (c) Random lasing threshold as a function of the Au NP diameter. The error bars enclose the standard deviation of the mean from 9 individual sample positions on 2 separately fabricated samples.

The effects of plasmonic NPs, embedded inside the doped nanofibers, on random lasing were characterized by comparing the lasing thresholds of different samples. Since the lasing threshold fluctuates across a single sample, we used a relative large pump spot (d = $280 \,\mu m$) to reduce the fluctuation and also average the threshold values measured in 9 positions (on a 3×3 grid with a grid spacing of 1 mm shown in Fig. 3). In addition, two samples, separately fabricated under identical conditions, were characterized for each Au NP size. The threshold was therefore determined by averaging over N = 18 individual measurements and the error was quantified by the standard deviation of the mean. The results presented in Fig. 3(c) show that the random lasing threshold is reduced by 17% in the presence of 10 nm Au NPs, as compared to the sample doped with only RHG dyes. The random lasing threshold increases for larger Au NPs. This can be explained by the spectral overlap between the dark-field scattering cross-section and the RHG fluorescence peak. As shown in Figure 1(d), the surface plasmon resonant peak of the 10 nm Au NPs is around 560 nm which is very close the peak emission of RHG dyes in the HPC network (i.e., the peak is at 553 nm). As a result, the plasmonenhanced light scattering in the nanofibers is the strongest for the 10 nm Au NP samples, leading to the shortest transport mean free path and the lowest lasing threshold.³⁴ Since the plasmon resonance of 80 nm Au NP does not coincide with the optical gain spectrum, the random lasing threshold is even higher than the one of undoped samples due to metal absorption.

In conclusion, we have developed an active nanofiber composite based on biodegradable HPC solutions and demonstrated random lasing with a reduced threshold due to plasmon-enhanced light scattering. Random lasing is optimized by tuning the localized plasmon resonance of Au NP into the gain spectrum. These findings provide an alternative and cost-effective approach for plasmon-enhanced random lasers based on a bio-degradable host matrix, which is particularly attractive for a number of biophotonic applications such as fluorescence sensing, optical tagging, and detection.

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