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Random laser spectroscopy for nanoscale perturbation sensing

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We report a spectroscopic method using coherent random lasers for a simple, yet nanoscale, sensing approach. Unique spectral properties of coherent random laser emission can be detectably altered when introducing nanoscale perturbations to a simple nanocomposite film that consists of dielectric nanospheres and laser-dye-doped polymer to serve as a transducer. Random lasing action provides a means to amplify subtle perturbations to readily detectable spectral shifts in multiple discrete emission peaks. Owing to several advantages, such as large-area detection, narrow and multiple emission peaks, straightforward detection, and simple fabrication, random laser spectroscopy has the potential for ultrasensitive, yet simple, biosensors in various applications. © 2010 Optical Society of America
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Sensitive and accurate assessment of subtle and minute perturbations such as nanoparticles and biomolecules is crucial for detecting diseases at early stages, for monitoring treatment responses, and for identifying threat agents in defense security applications. Although the recent advances in biological and chemical sensing are promising, they typically require complex fabrications and sophisticated detection strategies, which can potentially hamper widespread utilization and clinical translation. One interesting alternative approach is to take advantage of random lasing phenomena. In random lasers, spontaneous emission events can be significantly amplified through a long light path or deterministic laser cavities can be randomly formed due to multiple scattering in disorder gain media [1,2]. Since the exploration of discrete laser peaks in random media [3], random lasing effects have been widely studied in numerous material systems [4–9]. Recently, random lasing action—specifically, amplified spontaneous emission—has been used to detect explosives using intensity changes at a range of the emission wavelength [10,11]. More interestingly, random lasers with coherent feedback may have additional potential as biosensors: Narrow and multiple discrete peaks in emission spectra derived from a large number of resonant modes have been shown to be extremely sensitive to subtle perturbations in the system [2,5,6,8,12]. This characteristic in turn implies that the spectral properties of coherent random lasers can be exploited to assess nanoscale alterations as a potential spectroscopic modality. In this Letter, we report, for the first time to our knowledge, the concept of a novel spectroscopic method using coherent random lasing as a simple, yet nanoscale sensing mechanism.

To gain an understanding of the sensitivity limit of our method to nanoscale perturbations, we conducted numerical studies using a finite element method software package (Comsol Multiphysics 3.5a). Because of the limitation of computation resources, we modeled the random laser film as a two-dimensional disordered polymer waveguide with the corrugated surface formed by nanoparticles [6]. To mimic the experimental random laser

film, the refractive indices of the nanoparticle, the polymer film, and the substrate were set to be 1.45, 1.58, and 1.5, respectively. The thickness of the polymer waveguide and the radius of the nanoparticles were 800 nm and 75 nm, respectively. In our simulation, only TE polarization was modeled. Because hundreds of eigenvalues can be obtained numerically from the random laser film, and because only high-*Q* modes can lase experimentally, here we focused on high-*Q* modes at $\lambda \sim 680$ nm and ~ 689 nm.

To introduce experimentally detectable nanoscale changes, we randomly placed nanoparticles on the film

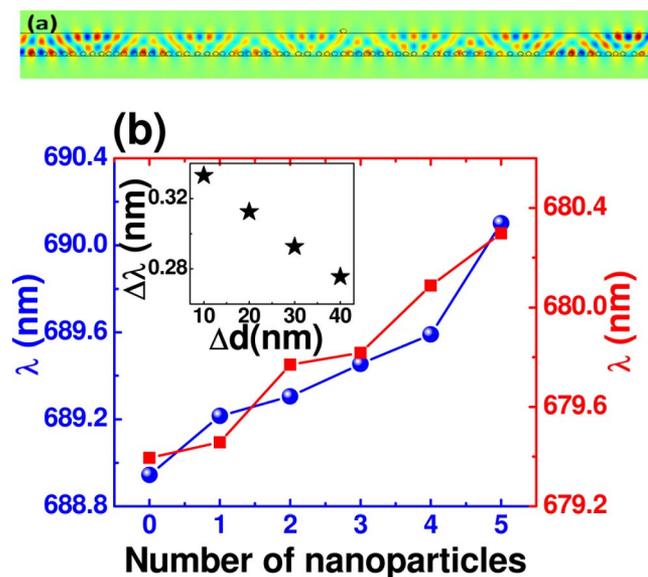


Fig. 1. (Color online) (a) Field distribution of the high-*Q* resonant mode in the disordered waveguide film with a single nanoparticle on the top surface. (b) Spectral shift of the resonant wavelength resulting from different numbers of nanoparticles on the top surface of the film. The blue dots and red squares are taken from different resonant modes at $\lambda \sim 680$ nm and ~ 689 nm, respectively. Inset, spectral shift of the resonant wavelength at the resonant mode of ~ 689 nm resulted from different binding locations of the single nanoparticle on the film (Δd is the distance from the original location).

and studied the corresponding spectral shift. Figure 1(a) shows that the field distribution of random lasing at the high- Q mode at $\lambda \sim 689$ nm is well confined in the disordered waveguide film with a single nanoparticle attached on the top boundary. We first tested the dependence of the resonant wavelength on the number of the nanoparticles that were randomly attached on the top surface. With the perturbation of nanoparticles, we can clearly see the spectral changes from the blue dots in Fig. 1(b). Adding one particle on the top surface can generate a wavelength shift of 0.2–0.3 nm, which can be easily resolved by a conventional spectrometer. As the number of the nanoparticles increases, the resonant mode keeps shifting to longer wavelengths. However, the relationship between the number of the nanoparticles and the wavelength shift is not linear, as shown in Fig. 1(b), given that the scatters are randomly distributed inside the simulated structure. As shown in the inset of Fig. 1(b), a slight change in the binding location can generate obvious shifts in the resonant wavelength. This is because the field distribution of the random laser resonances in the film is nonuniform. In other words, the energy scattered from the same nanoparticle can be totally different, depending on the binding location. Similarly, as different modes are usually confined in different positions in the random laser film, a different spatial distribution of the same nanoparticles can generate a different perturbation and result in a different spectral shift. The red squares in Fig. 1(b) show the dependence of the mode at ~ 680 nm, which has an overall similar trend to the blue dots, but with different details.

We further conducted pilot experiments to demonstrate the feasibility of random laser spectroscopy. We fabricated the random laser film consisting of a monolayer of silica nanospheres and a laser-dye-doped SU-8 polymer, similar to the previous study [6]. We first spin coated a single layer of silica nanospheres (radius $r = 75$ nm) on a microscope slide glass. The inset of Fig. 2(a) shows a representative scanning electron microscopy (SEM) image of the randomly distributed silica nanospheres on the microscope slide glass. Then, we coated dye doped SU-8 polymer onto the single layer of the silica nanospheres. For the laser dye, we used a high-quantum-efficiency laser dye, rhodamine 800. All the experimental parameters were similar to the numerical simulations.

Figure 2(a) illustrates our experimental setup. In brief, we optically pumped the film using a tunable pulse laser (an optical parametric amplifier pumped with a Ti:sapphire regenerative amplifier). The wavelength of the pump laser was 690 nm at the absorption peak of rhodamine 800. The pulse width was 100 fs, and the repetition rate was 1 kHz. We focused the pumping illumination to an area of $\pi \times 3.5^2 \mu\text{m}^2$ on the sample through a microscope objective (20 \times). The emitted light was collected by a fiber bundle through the same objective and a bandpass filter ($\lambda_{\text{center}} = 720$ nm and bandwidth $\Delta\lambda = 20$ nm), and coupled to a spectrometer (Acton Spectra-Pro150 and PIXIS CCD). A tilted nozzle was used to spray nanoparticles onto the top surface of the random laser film.

First, we tested lasing action in the random laser film itself. Figure 2(b) shows discrete peaks in the lasing

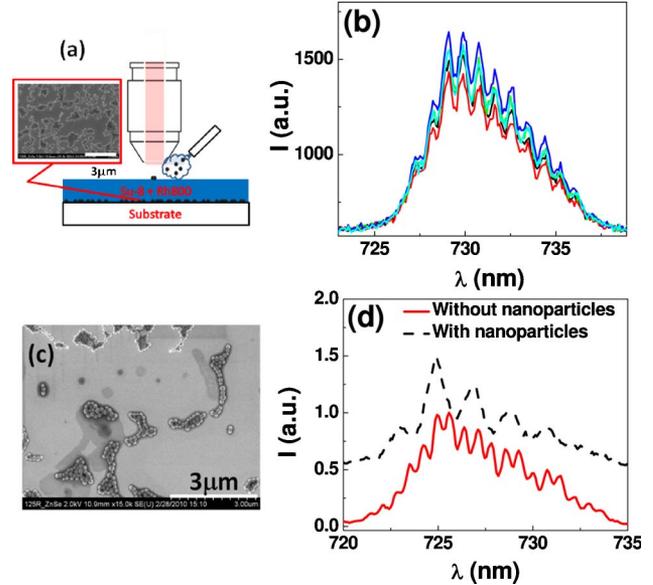


Fig. 2. (Color online) (a) Schematic illustration of our optical setup. Inset, SEM image of randomly distributed silica nanoparticles on a glass substrate before applying SU-8 polymer on it. (b) Spectra of random lasing emission from the random laser film measured over time. Each acquisition time is 1 s averaged over ~ 500 pumping pulses. (c) SEM image of silica nanoparticles attached to the top of the random laser film. (d) Changes in the emission spectrum before (red solid line) and after (black dashed line) introducing the nanoparticles.

spectra at the pump power of 0.5 mW (we kept the same pumping power for all the following experiments). The laser linewidths of ~ 0.2 nm, which was limited by the spectral resolution of our spectrometer, were several orders of magnitude narrower than that of the spontaneous emission of rhodamine 800. We also observed a laser threshold behavior in our film. This relatively simple nanocomposite film can exhibit low optical loss and high gain as an ideal material for a random laser. More importantly, we confirmed the spectral stability of the random laser emission over time, which is a critical requirement for random laser spectroscopy. The different lines in Fig. 2(b) were the lasing spectra recorded over different time points from the same position with the same pumping power and the acquisition time for each spectrum was 1 s, averaged over 500 pulses. There were no obvious changes in the discrete peak positions, while the overall intensity could be slightly varied. Such spectral stability in random lasing emission is in good agreement with other previous studies [13,14].

Then, we studied changes in the laser spectra by spraying nanoparticles (silica nanospheres of $r = 75$ nm) on the top surface of the random laser film, while keeping all the other conditions the same. We quantified the number of the nanoparticles on the film using SEM images from the pumping area as shown in Fig. 2(c). Figure 2(d) shows that the black dashed random laser spectrum is significantly changed, compared to the original spectrum (i.e., the red solid line). The dramatic changes in the number of the laser peaks, the peak positions, and the peak linewidths indicate that the overall resonant properties were completely changed in this system. The following

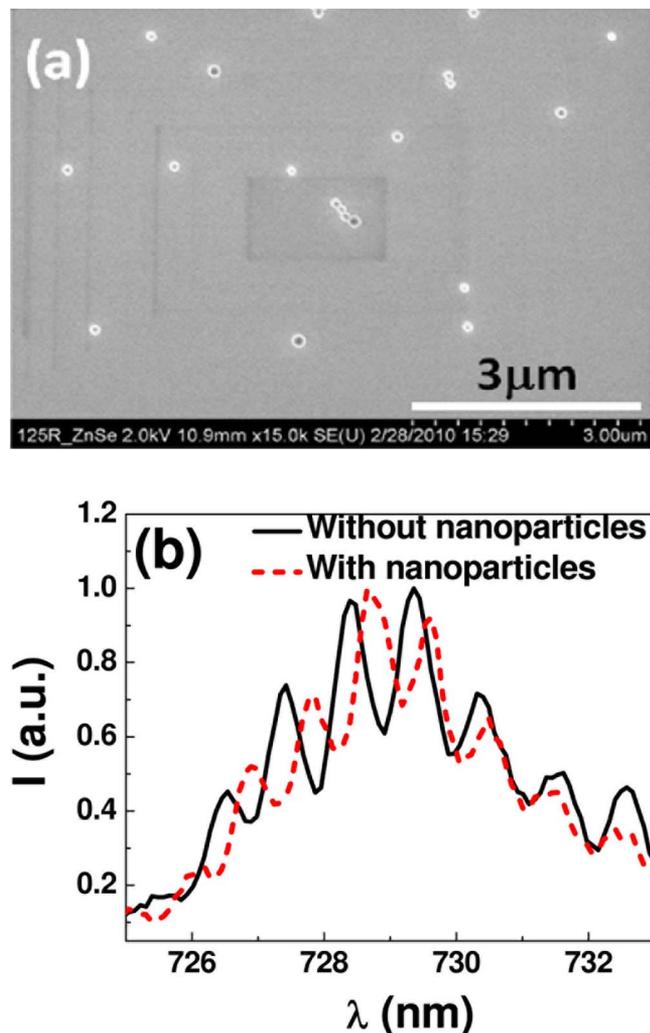


Fig. 3. (Color online) (a) SEM image of 20 silica nanoparticles attached to the film. (b) Changes in the emission spectrum before (red solid line) and after (black dashed line) introducing the nanoparticles.

SEM characterization confirmed that more than 300 nanoparticles can be observed in the detection area.

We further decreased the number of nanoparticles on the film and acquired corresponding spectra changes. The SEM image in Fig. 3(a) showed that there were merely ~ 20 silica nanoparticles attached in the pumping area. Figure 3(b) depicts clear spectral shifts in each discrete peak resulting from the particle binding, while the overall spectral shape and the total number of the discrete peaks were almost the same. This can be easily understood as follows: Because the peak separation is extremely narrow, if the peaks are generated from a single resonator, the corresponding gain length will be several hundred micrometers, which is far greater than the actual pumping size of $\sim \pi \times 3.5^2 \times 0.8 \mu\text{m}^3$. Thus, each peak should be generated from different resonators and sense different perturbations of nanoparticles, as shown in Fig. 1(b). We note that this experimental sensitivity of ~ 20 nanoparticles in the area of $\pi \times 3.5^2 \mu\text{m}^2$ (the corresponding mass $\approx 9.2 \times 10^{-14} \text{ g} = 1.5 \times 10^{-15} \text{ mole}$) was limited by the spectral resolution of our spectrometer and the nozzle system.

Random laser spectroscopy has potential advantages as bio/chemical sensing mechanisms over conventional approaches: 1) As random lasers are usually formed by spatially extended modes [12,13], they can provide a large detection area; 2) linewidths of laser peaks above the laser threshold are extremely narrow with multiple discrete peaks, potentially increasing signal-to-noise ratio; 3) as the signal can be detected in the far field, no precise alignment of the system is required for random laser detection; 4) the fabrication of the random laser film is simple and cost-effective; 5) by detecting a spectral change compared with a reference spectrum, it does not require *a priori* information about agents and allows continuous detection and monitoring.

In conclusion, we have investigated the possibility of random laser spectroscopy and demonstrated that the unique spectral properties of coherent random lasers could potentially be utilized for potential biological and chemical sensing methods. We fabricated fairly simple nanocomposite polymer films consisting of silica nanoparticles and rhodamine 800-doped SU-8 polymer as a transducer, which provides gain media and scatterers for random lasing effects. Our experimental results showed that the spectroscopic method can at least detect a structural change resulting from ~ 20 silica nanoparticles. Owing to the potential advantages of random lasing effects, it will be possible to develop effective sensing methods that allow label-free, large-area, and cost-effective detection, while offering unprecedented sensitivity and reliability.

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