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Coherent Random Lasing Realized in Polymer Vesicles

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Abstract: We have demonstrated the realization of a coherent vesicle random lasing (VRL) from the dye doped azobenzene polymer vesicles self-assembled in the tetrahydrofuran-water system, which contains a double-walled structure: a hydrophilic and hydrophobic part. The effect of the dye and azobenzene polymer concentration on the threshold of random laser has been researched. The threshold of random laser decreases with an increase in the concentration of the pyrromethene 597 (PM597) laser and azobenzene polymer. Moreover, the scattering of small size group vesicles is attributed to providing a loop to boost the coherent random laser through the Fourier transform analysis. Due to the vesicles having the similar structure with the cell, the generation of coherent random lasers from vesicles expand random lasers to the biomedicine filed.

Keywords: Random laser; vesicles; scattering; azobenzene polymer

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1. Introduction

V. S. Letokhov theoretically proposed random lasers (RLs), which have been realized in the disordered gain medium based on light being amplified due to the multiply light scattering as a feedback cavity [1]. Due to its unique features, e.g., low cost, small size, easy integration, and low spatial coherence [2–4], the random laser is drawing much attention in disorder photonics [5–8]. The key element of traditional lasers includes a resonator cavity, which is usually composed of several mirrors to feedback the amplified light. Different from the traditional lasers, the RLs do need the fussy resonator cavity to be a feedback medium, which only relies on the multiply light scattering to form a random loop, and thus, it can simplify the structure of RLs [9–13]. In order to make the threshold lower, the fiber random laser has been developed [14–16].

Recently, azobenzene containing amphiphilic

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polymers which can self-assembly to form colloidal size aggregates or vesicles has attracted considerable attention [17–20]. The polymer vesicles have been applied in the targeted drug delivery [21], contrast enhanced imaging [22], and mimic for biological membranes [23]. Moreover, polymer vesicles have lots of excellent properties, such as good compatibility with cells [24] and good resolvability in aqueous [25–28], organic, and aqueous organic mixtures [29, 30], which can be applied in the biomedical field. The light emission from the vesicle can be achieved by integrating the luminescent entity in the vesicle or its membrane. The light emission of the vesicles can also occur through nonlinear processes at the vesicle membrane interface, such as the second harmonic scattering (SHS), coherent Raman scattering, and sum-frequency scattering (SFS). The non-linear effect arises from the intrinsically nonlinear response of the membrane due to the incorporation of photochromophores.

Due to the possibility of biocompatibility through the selection of suitable materials, luminescence vesicles have been found for many applications in bio-imaging. Some researchers [31–33] have shown that, putting incorporation of azo chromophores into the self-assembly system of amphiphilic polymers can be further extended to new areas of the material design and preparation. W. Su has successfully fabricated the micron polymeric vesicles containing azobenzene groups by the control of self-assembly and studied the light-induced behavior of vesicles [34, 35]. To explore new forms of photochemical combination therapy, F. Lahoz *et al*. have demonstrated that chemically modifying anticancer drugs can provide random lasing (RL) when infiltrated in a biological tissue [36]. M. Humar *et al*. fabricated microbeads with poly(lactic-co-glycolic acid) and poly(lactic acid)-substances approved for the medical use and demonstrated lasing from the tissues and whole blood [37]. The implanted lasers may enable real-time monitoring of physiological information, such as temperature. In 2011, M. C. Gather *et al*. first reported the successful realization of biological cell lasers and obtained a high-Q microcavity producing bright, directional, and narrow-band laser emission in the green fluorescent protein [38]. More and more researchers are linking RLs and biomedicine skillfully to achieve major breakthroughs in the medical field. The vesicles can be considered as a candidate matrix for RL in the biological photonics because its structure is similar to that of the cell.

In this work, we fabricate the coherent random lasing emission from the dye-doped vesicle with the cell-like structure, which is self-assembled from the azobenzene polymer with hydrophilic and hydrophobic parts in the tetrahydrofuran-water (THF/H_2O). There are two different size groups in the vesicle self-assembly solution, which are 3 μm – 5 μm (large size group, LSG) and 0.5 μm – 1μm (small size group, SSG), respectively. From the Fourier transform, we calculate the smallest resonant cavity to be 4.2μm which is smaller than the size of LSG. Therefore, the multiply scattering of RLs can be attributed to the scattering from SSG. In addition, we study the effect of the concentration of dye and azobenzene polymer on the emission and threshold of RLs.

2. Materials and methods

There are two isomeric structures in the azo group. One is a trans structure where the molecule is rod-shaped, and the other is a cis structure in one plane where the whole molecule has a turn-like structure, and the two benzene ring planes are vertical on the plane where CN=NC is located. The polymer vesicles prepared by the amphiphilic block copolymer self-assembly method are usually hollow spheres with a hydrophobic membrane and a hydrophilic inner and outer canopy in the aqueous solution. For relatively weak stimuli, these vesicles can control reactions such as shape changes,

aggregation to other types of aggregation, and dissociation. Figure 1(a) shows the self-assembly process of dye doped vesicles, which includes 0.104 wt.% azobenzene polymer and 0.078 wt.% dye in the THF/H_2O system. In order to avoid the effects of laser dyes in the solution on random lasers, we dialysis the solution in which the THF and aqueous solution at a ratio of 3:5 is used. Then, the dialysate is changed every three hours, until dialysate becomes transparent. Figure 1(b) represents the molecular structures of the azobenzene polymer-poly (N-isopropylacrylamide)- Blocks-Poly [4'-(4-benzoylphenyl alanine methyl azo phenyl) phenyl methacrylate] [PNIPAM-b-P(Azo-Phe)] which consists of a hydrophilic part PNIPAM and a hydrophobic part P(Azo-Phe). Due to the copolymer with the high content of hydrophobic units of P (Azo-Phe) block, the copolymer cannot be directly dissolved in water, and thus, THF is chosen to facilitate the self-assembly as a common solvent [39, 40]. When water is gradually added into the THF solution, PNIPAM-b-P(Azo-Phe) chains start to associate with each other in the solution due to the hydrophobic interaction. Optical gain is provided by PM597 whose molecular formula is shown in Fig. 1(c).

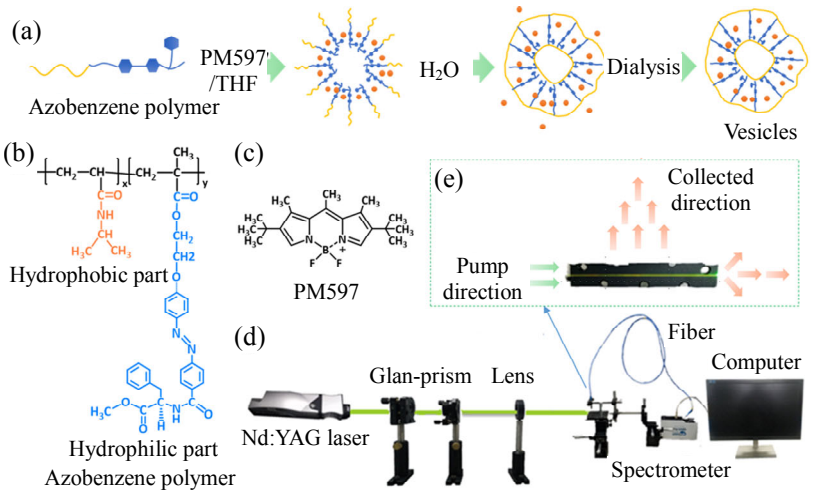


Fig. 1 Vesicles material structure and random lasing experimental setup: (a) self-assembly process of dye doped vesicles, (b) molecular structures of the azobenzene polymer, (c) molecular structures of PM597, (d) setup of the random lasing measurement, and (e) pump direction and the collected direction.

Figure 1(d) shows the measurement schematic diagram of random lasing for the vesicle samples. A *Q*-switched Nd:YAG laser with a round spot (duration of 10 n and repetition rate of 10 Hz) outputs the wavelength of 532 nm to pump the dialyzed vesicle solution samples filled in the glass tube through a convex lens with *f* of 10 cm. The pump pulse energy and polarization are controlled by a Glan prism group. The emitted light is collected by a fiber spectrometer (QE65PRO, ocean optics, resolution of ~0.4 nm and integration time of 100 ms). As shown in Fig. 1(e), the solution samples are pumped along the waveguide direction and the emitted light is obtained by the fiber spectrometer in the direction of the vertical waveguide.

The absorption change of the azopolymer vesicles due to cis-trans isomerism transformation under the ultraviolet (UV) and visible light irradiation is shown in Fig. 2. Figure 2(a) shows the schematic diagram of photo-induced isomerization of the vesicles. Figure 2(b) is the absorption spectrum of the measured solution under UV light. There is a broad absorbance in 313 nm – 399 nm with the main peak centered at 359.6 nm for the

vesicles. Under the irradiation of UV light of 365 nm, the absorption decreases rapidly in the 10 s – 20 s and then decreases slowly between 30 s and 50 s due to the absorption of trans-isomer units at about 365 nm. And then the absorption spectrum of the vesicles solution under visible light is shown in Fig. 2(c). Under a visible light irradiation, the absorption intensity at 359.6 nm increases rapidly in the 10 s – 20 s and increases slowly to the original intensity before the UV irradiation in 185 s, which proves that the cis-isomer has transformed the trans-isomer.

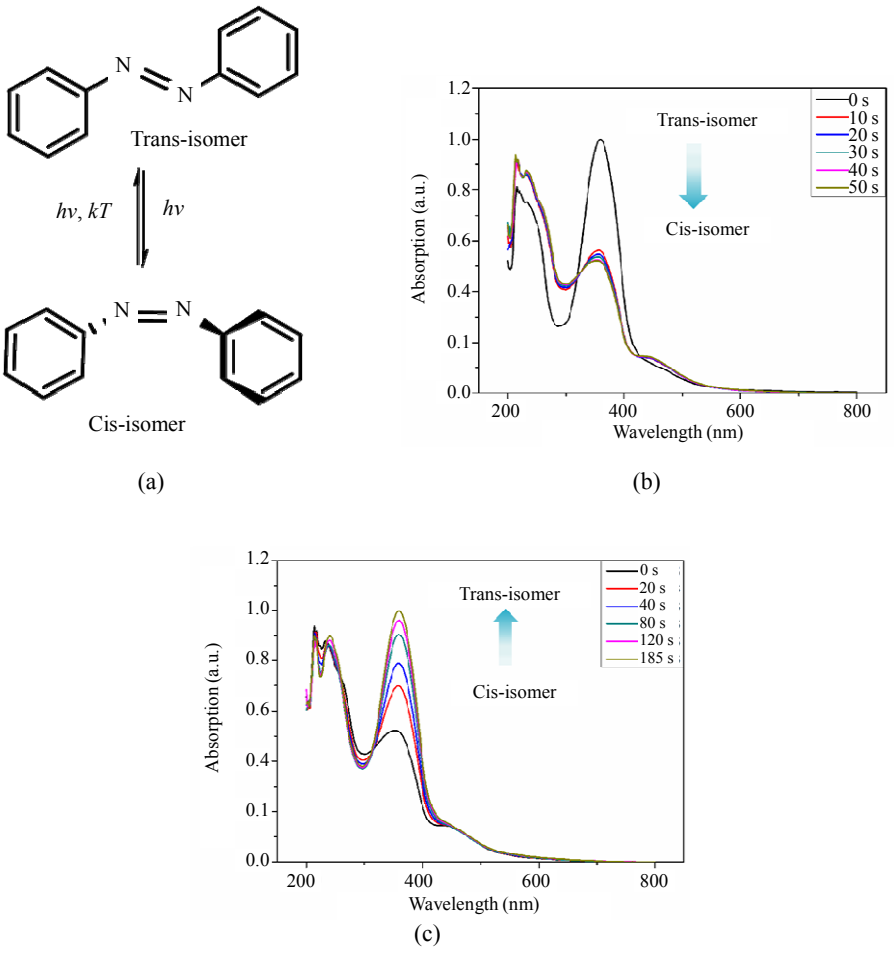


Fig. 2 Cis-trans isomerism: (a) photo-induced isomerization of the vesicles, (b) absorption spectra of the vesicles under UV irradiation, and (c) visible of light irradiation.

Figure 3 shows the images of vesicles under the optical microscope, transmission electron microscopy (TEM), and the confocal laser scanning microscopy (CLSM). It can be seen that the shape of the vesicle is approximately circular and the dye dopant does not damage the formation the vesicles. Figures 3(a) and 3(b) show the microscope images of vesicles without and with the dye dopant. Most vesicles belong to the small size group (SSG) with the diameter of 0.5 μm – 1 μm, while only a small part of the vesicles belongs to the large size group (LSG) with the diameter of 3 μm – 5 μm. The characterized vesicles which are undoped and doped with dye by TEM are shown in Figs. 3(c) and 3(d), respectively. Figures 3(e) and 3(f) show the bottom and middle parts of the vesicles through CLSM. From Fig. 3, it is evident that the assembly shape of vesicle is circular.

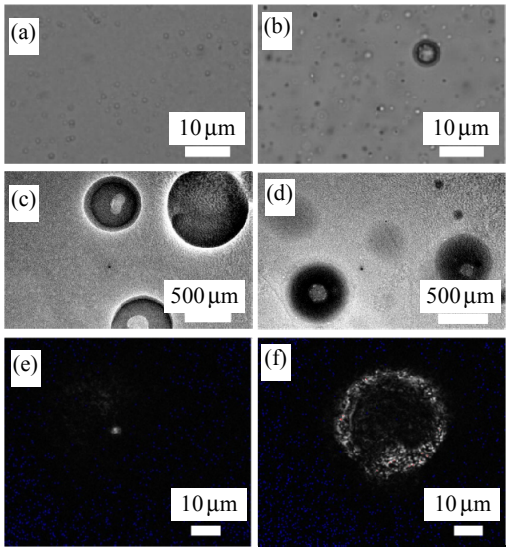


Fig. 3 Vesicles images: microscope image of vesicles (a) with and (b) without the dye dopant, and TEM images of vesicles (c) with and (d) without dye dopant. The CLSM image of the vesicle composed of PNIPAM-b-PAzPy2 with dye from (e) the bottom slice to (f) the middle slice of the vesicle.

3. Results and discussion

In order to study the effect of dye concentration on random lasers, random lasing spectra of 0.156 wt.%, 0.234 wt.%, and 0.312 wt.% dye doped vesicles can be shown in Figs. 4(a), 4(c), and 4(e) while the concentration of azo polymer is 0.104 wt.%. Figures 4(a), 4(c), and 4(e) show that the lasing intensities increase with increasing pump energy. For the pump energy below 233 μJ, 123 μJ, and 17.81 μJ, weak and extensive spontaneous emissions from the solution samples can be observed. When the pump energy reaches 233 μJ, 123 μJ, and 17.81 μJ, respectively, the initial sharp peaks occur from the broad emission, and their intensity increases significantly with the pump energy. Under 532 nm pump light, we observe that the wavelengths of the highest peaks in the spectrum are 590.64 nm, 587.86 nm, and 600.36 nm, respectively. The non-linear variations between the input and output energies of the lasing peak are shown in Figs. 4(b), 4(d), and 4(f). The apparent transition from the spontaneous emission to stimulated emission and a non-linear increase in the emission intensity demonstrate the lasing emission action, and the thresholds of the lasing are approximately 233 μJ, 123 μJ, and 17.81 μJ. What's more, it is clear that with the concentration of laser dye increasing, the threshold significantly decreases, which is caused when the light gain becomes stronger and the pump energy required for obtaining a random laser light becomes smaller, thus the threshold value becomes smaller accordingly.

To further investigate the characteristics of the random laser, we measure the lasing emission emitted at different concentrations of azo polymer. A schematic diagram of the measurement system is shown in Fig. 1(d). Figure 5 shows the effect of the concentration of the azo polymer on the random lasing threshold with the same dye concentration of 0.078 wt.%. Figures 5(a), 5(c), and 5(e) describe random lasing spectra of vesicles with 0.156 wt.%, 0.208 wt.%, and 0.312 wt.% azo polymers, respectively. As can be seen from the figure, with an increase in the concentration of the polymer to form more vesicles, which causes the vesicles system a strong scattering, the threshold is gradually decreasing.

To verify the random lasing source for the dye doped vesicles, we analyze the Fourier transform of the emission spectrum of the vesicle solution with different dye and azo polymer concentrations at a pump energy of 500 μJ. In the Fourier transform of a laser cavity emission spectrum (separated by wave vector $k=2\pi/\lambda$, λ is the emission wavelength), there are spikes peaks at P_m and satisfy the following relationship:

$$P_m = \frac{mnL_c}{\pi}$$

where m is the Fourier series number, n is the refractive index of the gain medium, and L_c is the cavity path length.

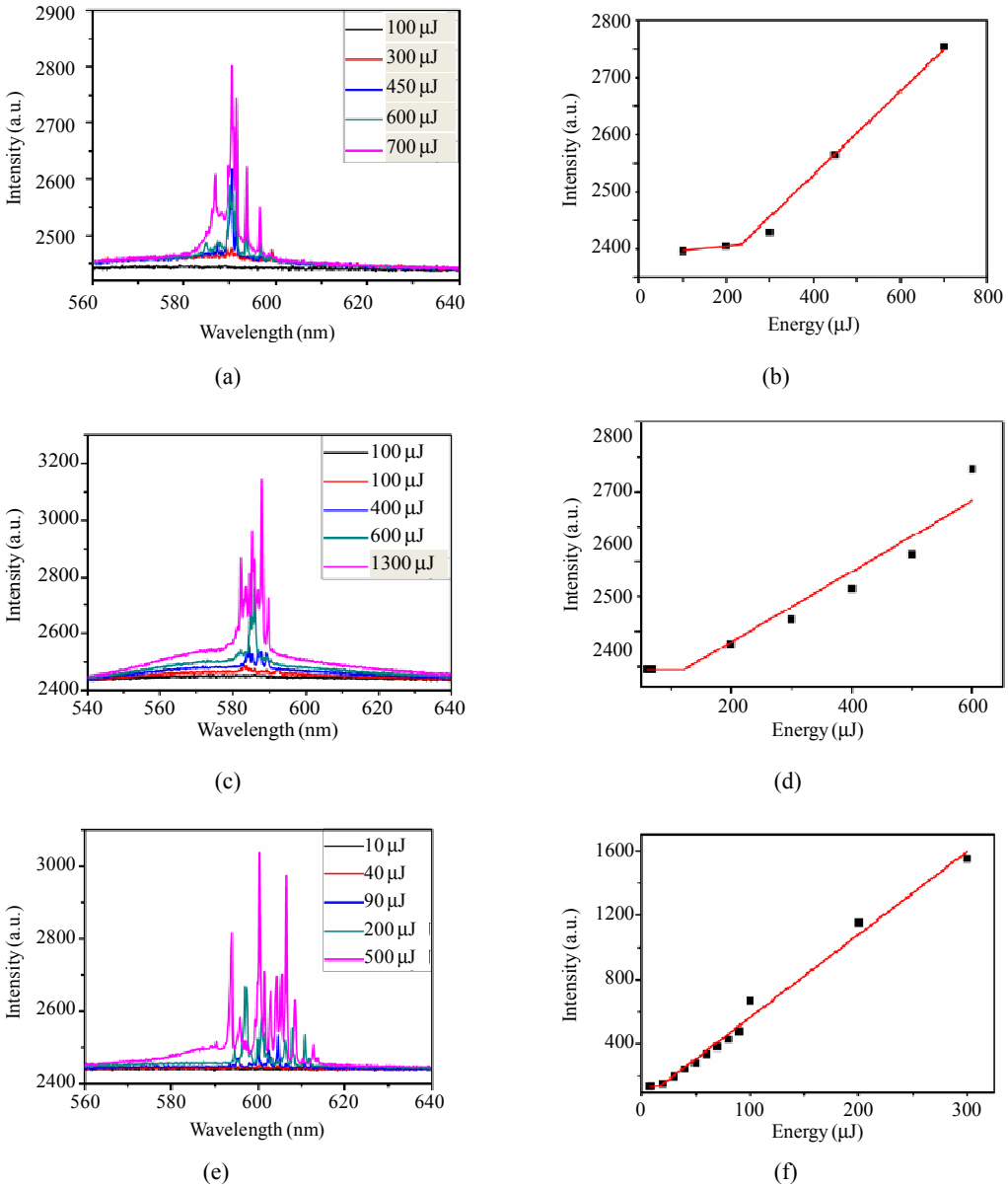


Fig. 4 Random lasing spectra at different energy pumps for (a) 0.156 wt.%, (c) 0.234 wt.%, and (e) 0.312 wt.% dye doped vesicles; and the input-output relation corresponding to the above (b–f) cases.

Obviously, sharp emission peaks in the emission spectrum cause well-separated peaks in the Fourier transform, as shown in Figs. 6(a), 6(b), 6(c), 6(d), 6(e), and 6(f). According to the above formula and the first peak (m=1) in the Fourier transform spectra P=1.82 μm, 1.83 μm, 5.13 μm, 2.19 μm, 14.29 μm, and 1.82 μm for the Figs. 6(a), 6(b), 6(c), 6(d), 6(e), and 6(f), we obtain L_c =4.20 μm, 4.23 μm, 11.84 μm, 5.06 μm, 33.99 μm, and 4.20 μm for the corresponding cases. As can be seen from Fig. 3, the largest vesicles are 3μm – 5 μm and the smallest vesicles are 0.5 μm. By the Fourier transform, we calculate the smallest resonant cavity to be 4.20 μm. This suggests that the vesicle random lasing (VRL) is not caused by the scattering of a single vesicle, but the multiple scattering of SSG vesicles forms a closed loop, as shown in the Fig. 7.

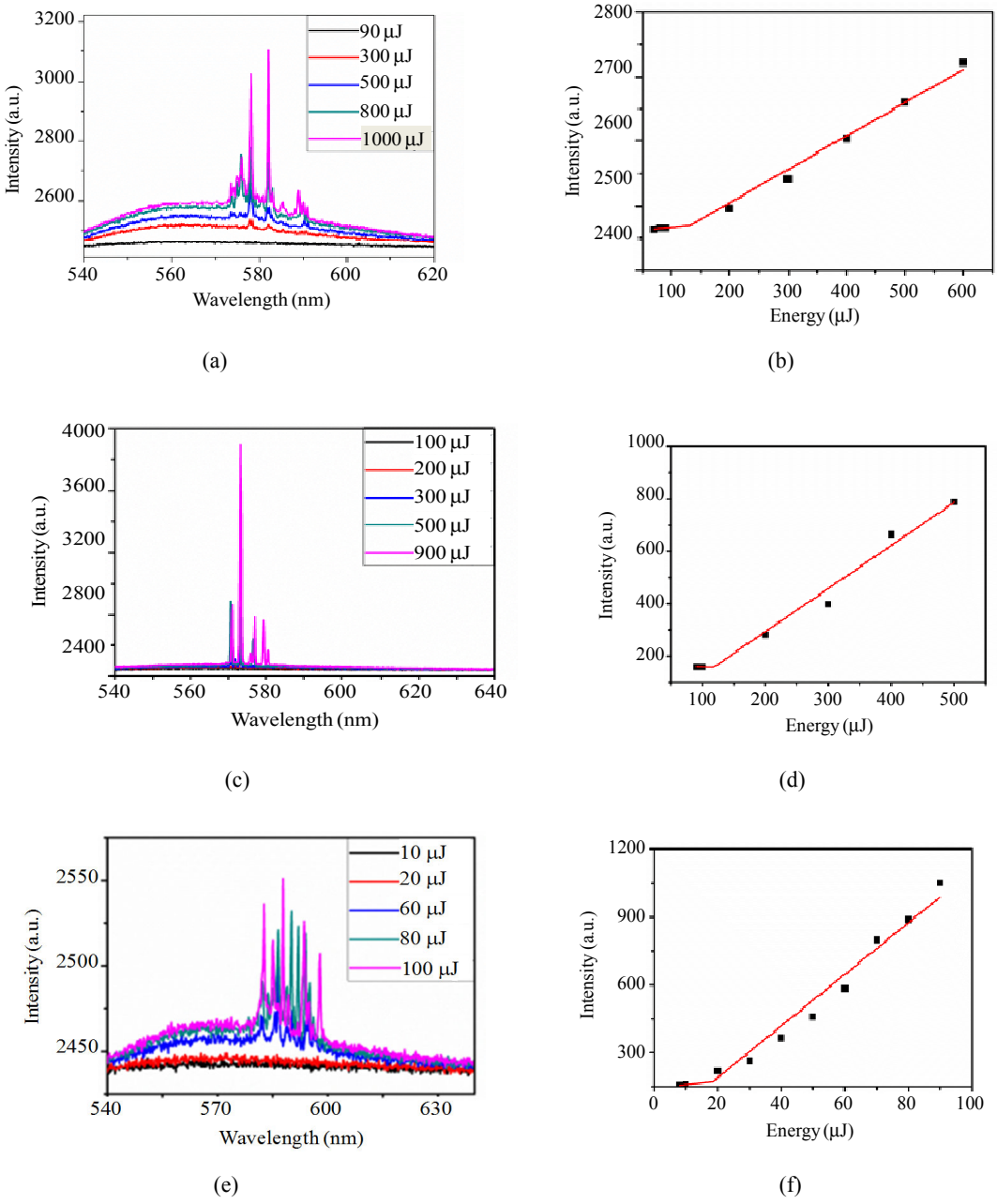


Fig. 5 Random lasing spectra at different pump energies for (a) 0.156 wt.%, (c) 0.208 wt.%, and (e) 0.312 wt.% azo polymers; and input-output relation corresponding to the above (b–f) cases.

Figure 8(a) shows the random laser spectra of the vesicles solution at different pump pulse times with pump energies of 500 μJ. The peaks of P_1, P_2, P_3, P_4, P_5, and P_6 corresponding random lasing wavelengths of 571.16 nm, 573.18 nm, 576 nm, 576.73 nm, 579.3 nm, and 580.59 nm are relatively stable. However, there are ~0.06 nm blue-shift relative to the wavelength of P3 from 576.1 nm to 576.04 nm for the second time which is in the range of resolution error. Meanwhile, it is obvious that the random lasing intensity fluctuates under different pulse pumps, which is caused by the vesicles disorder system with the stochastic cavity. Moreover, in order to better observe the stability of the VRL, we perform a Fourier transform on the random laser spectrum. As shown in Fig. 8(b), not only most

wavelength locations of the random laser remain in the same position, but also the Fourier transform length remains the same value. Therefore, the stable VRL in the wavelength has been obtained.

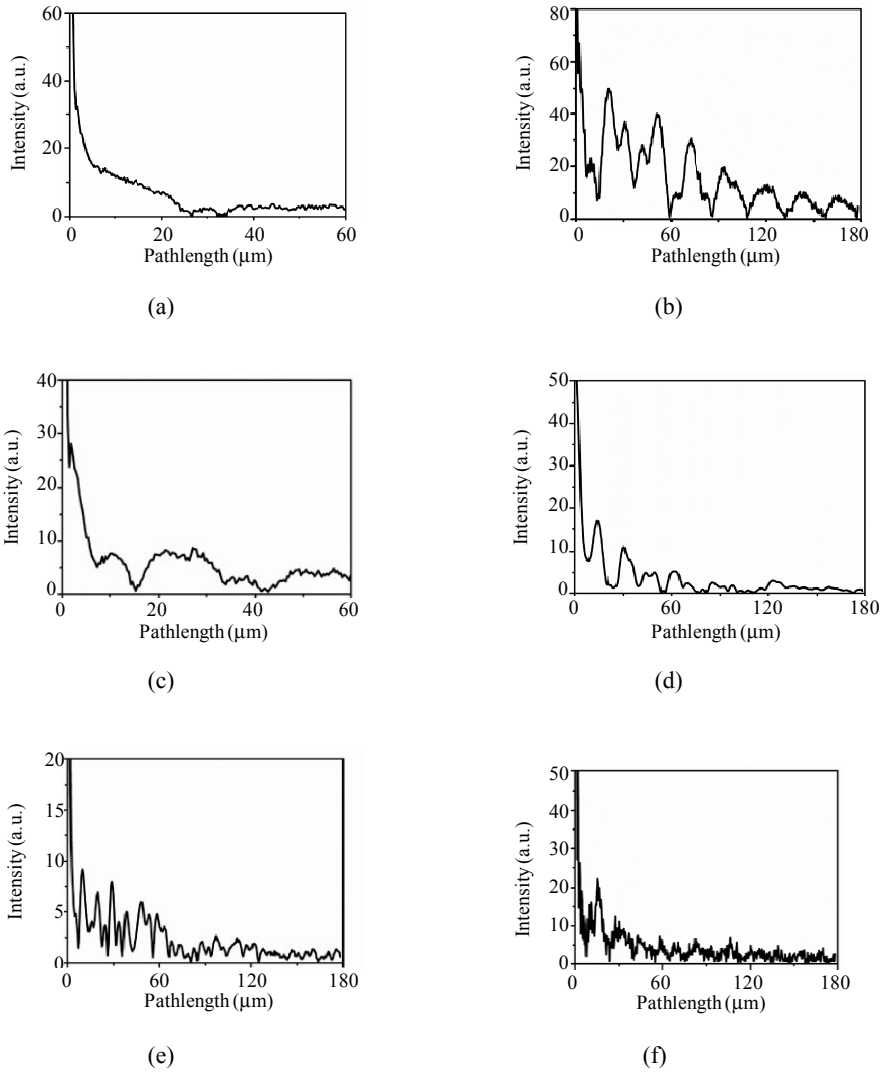


Fig. 6 Fourier transform corresponding the emission spectra of (a) 0.156 wt.%, (b) 0.234 wt.%, and (c) 0.312 wt.% dye doped vesicles in Figs. 4(a), 4(c), and 4(e), and (d) 0.156 wt.%, (e) 0.208 wt.%, and (f) 0.312 wt.% azo polymers in Figs. 5(a), 5(c), and 5(e).

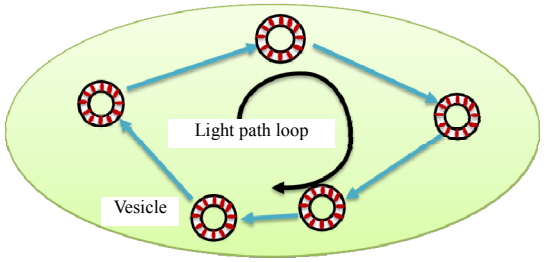
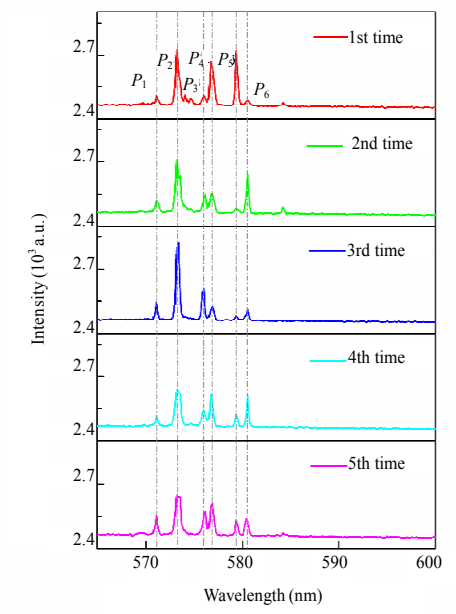
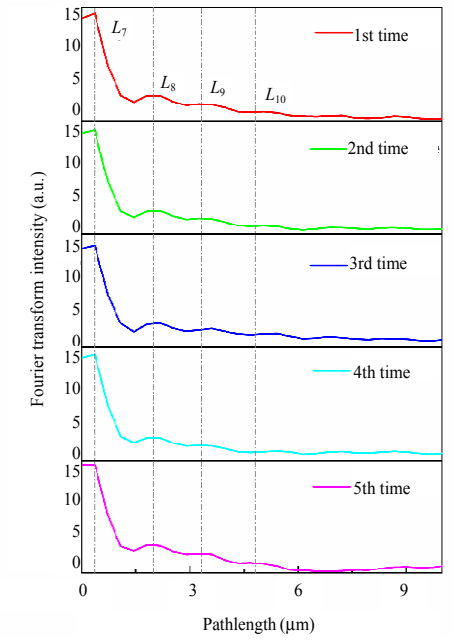


Fig. 7 Multiple scattering mechanism diagram ofvesicles.



(a)



(b)

Fig. 8 Random lasing emission and Fourier transform: (a) random laser spectra of the vesicles solution at different pump times with the same pump energy of ~500 μJ and (b) Fourier transform corresponding to the emission spectrum.

4. Conclusions

To conclude, this work systematically demonstrates the form of dye-doped azobenzene polymer vesicles and realization of coherent random lasers. And we study the effect of the concentration of the dye and azobenzene polymer on the random laser. From the Fourier transform analysis, we prove that the coherent random lasing source of dye-doped vesicles is from the small size group muti-scattering. This work paves a way on how to design a vesicle random lasing and expand the random laser to be applied in biological photonics.

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