Resonance-driven random lasing

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A random laser is a system formed by a random assembly of elastic scatterers dispersed into an optical gain medium[1]. The multiple light scattering replaces the standard optical cavity of traditional lasers and the interplay between gain and scattering determines the lasing properties. All random lasers studied to date have consisted of irregularly shaped or polydisperse scatterers, with a certain average scattering strength that was constant over the frequency window of the laser[2–4]. In this letter we consider the case where the scattering is resonant. We demonstrate that randomly assembled monodisperse spheres can sustain scattering resonances over the gain frequency window, and that the lasing wavelength can therefore be controlled by means of the diameter and refractive index of the spheres. The system is therefore a random laser with an *a priori* designed lasing peak within the gain curve.

In recent years the interest in random lasing has grown very rapidly, particularly following the observation of this phenomenon in powdered laser crystals[5], ceramics[6], organic composites[7], and even biological tissue[8]. The necessary condition for a random laser is that the material is multiply scattering light, which means that the transport mean free path (the average distance over which the scattered light direction is randomized) $\ell_t \ll L$, where L is the sample size. The other fundamental quantity is the gain length ℓ_g, which represents the path length over which the intensity is amplified by a factor e^{+1}. The interaction between gain and scattering determines the unique properties of the random laser and, in particular, defines the critical thickness for the sample (in slab geometry) to lase, $L_{cr} = \pi\sqrt{\ell_g \ell_t/3}$ (ref. 9). Unlike in ordinary lasers, the resulting light emission is multidirectional, but the threshold behaviour[3], the photon statistics[10,11] and relaxation oscillations[12,13] are very similar to those of standard lasers. The spectral output of a random laser system contains narrow emission spikes[4], which for large spectral width can merge into a smooth peak with an overall narrowing of the spectrum in most experimental configurations[3,14], like the one considered in this paper.

Wavelength tunability is a crucial property of lasing devices. In regular lasers this is easily achieved by tuning the resonance frequency of the resonator. The same principle has also been applied in more complex cavity structures, such as distributed feedback lasers and photonic crystals lasers, in which the cavity modes are the Bloch modes associated with the periodic structure. Tuning the lattice constant then provides a simple tool to tune the laser for high-quality photonic crystals[15,16] or with localized periodicity[17,18]. These tricks do not work in random structures due to the absence of periodicity. Here we will show, however, that even in a completely random system with no periodicity, resonant tunability can be achieved based on single-particle resonances.

A random system, composed of particles of arbitrary shape and size, has a transport mean free path that is nearly spectrally flat (nonresonant), at least over a wavelength range of ~100 nm. Under this condition, conventional random lasing occurs at a wavelength where $\ell_g(\lambda)$ has its minimum; that is, at the maximum of the gain curve. To obtain a random system where lasing modes can be selected at specific wavelengths, we propose to make use of a medium with resonances in the transport parameters. Our idea is to exploit the resonances in scattering coefficients, called Mie resonances[19], that are present when the sizes are comparable with the wavelength of the incident light, which can be easily achieved for regularly shaped resonators such as disks, cylinders or spheres. In a random assembly of such identical scatterers, the resonances survive as peaks in the transport parameters, and in particular in $\ell_t(\lambda)$. We chose monodisperse polystyrene spheres as constituents of a three-dimensional, solid random system that we have dubbed 'photonic glass'[20] (see Methods). Here we report on the random lasing action from such photonic glasses. The resonant nature of $\ell_t(\lambda)$ selects the lasing energy. We experimentally demonstrate that the lasing wavelength becomes very sensitive to the diameter, d, of the constituent spheres and follows the resonances of the system. In a system with a broad gain curve we managed to observe mode competition this way, because we were able to access more than one resonance with comparable gain.

Self-assembly of monodisperse spheres is the technique most commonly used to grow direct opals[21]. To obtain a disordered packing of spheres a modified self-assembly method has been developed (see Methods). The photonic glass obtained in this way was used as the basis of an amplifying system by embedding dry organic laser dye. To that end, 4-dicyanomethylene-2-methyl-6-p-dimethylaminostyryl-4H-pyran (DCM) special was dissolved in pure ethanol and the solution was infiltrated into the photonic glass. Complete ethanol evaporation was assured by gently heating the sample. The amount of DCM was 0.3 wt% for all samples considered here; this was verified by comparative weight measurements.

A scanning electron microscope (SEM) image of such photonic glass is depicted in Fig. 1a. Autocorrelation of the SEM image of the surface and cleaved edge revealed a completely disordered system without positional correlation[20]. Static and dynamic measurements of the photonic glass light transport have shown matching resonances for $\ell_t(\lambda)$ and the diffusion constant of light $D(\lambda)$ (ref. 22). In Fig. 1b–d, transmission measurements are

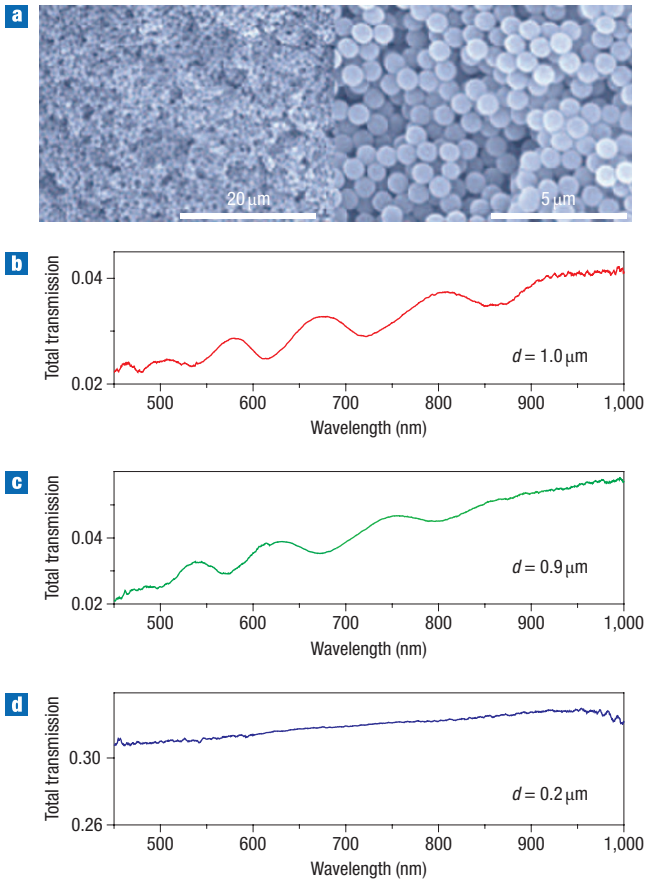

Figure 1 Static measurements of the photonic glass light transport. a, SEM image of a photonic glass with a filling fraction of ~0.55 and $d = 1.22$ μm. **b–d**, Total transmission for photonic glasses with $d = 1.0$ μm, 0.9 μm and 0.2 μm, respectively. The polydispersity for all the samples is ~2%. The total integrated transmission was measured with an integrating sphere, upon white light illumination.

plotted for glasses with the same filling fraction, but with different sphere diameters. The total transmission for a random system with a slab geometry is expressed by Ohm's law[23,24], which states that the total transmission $T(L, \lambda) \propto \ell_t(\lambda)/L$. Therefore a measurement of $T(L, \lambda)$ is a direct probe of the spectral dependence of $\ell_t(\lambda)$. For the samples of Fig. 1b, c, Mie resonances are pronounced and in complete phase opposition, even if the difference in the diameter is only ~0.1 μm. As a reference we consider a glass of very small spheres with $d = 0.2$ μm (Fig. 1d) that does not show any resonances, because the diameter is too small to sustain resonances in the visible range. The multiple light scattering condition was ensured by using samples of thickness L larger than 100 μm, which is much bigger than the typical mean free path in such photonic glasses ($\ell_t \approx 2$–3 μm for visible light, see Supplementary Information, Fig. S1).

The lasing process in a random laser can be described, to a first approximation, with the rate equations of the laser medium[25]:

$$\frac{dN_1(t)}{dt} = P(t) - \frac{\beta q(t) N_1(t)}{\tau} - \frac{N_1(t)}{\tau},$$
$$\frac{dq(t)}{dt} = \frac{\beta N_1(t)}{\tau}[q(t)+1] - \frac{q(t)}{\tau_c}, \qquad (1)$$

where $N_1(t)$ is the number of excited molecules, $P(t)$ is the pump rate, $q(t)$ the number of photons in laser modes, τ the spontaneous emission lifetime of the dye, and β is the β-factor for a random laser that involves the average numbers of lasing modes[26] . From the solution of the diffusion equation, the mean value of the cavity-decay time τ_c can be derived[27] and found to depend on $D(\lambda)$, $\tau_c = L^2/8D(\lambda)$. From equation (1) it is then evident that the threshold and laser process can be controlled by modifying $D(\lambda)$ and hence $\ell_t(\lambda)$.

The optical excitation for the photonic glass laser was obtained using a frequency-doubled Q-switched Nd:YAG source, with a 10 Hz repetition rate. The spot size was fixed at 1 mm diameter, to access a large gain volume. The diffuse emission was monitored with a spectrometer with a resolution of 0.5 nm. Plots for the resonant random laser above threshold are depicted in Fig. 2a, together with the dry-dye fluorescence. In the experiment we used four different photonic glasses, with the same filling fraction (55%) but with different sphere diameter. The reference sample with $d = 0.2$ μm (blue line) and the polydisperse TiO_2 (dotted cyan line) lase at nearly the same wavelength, close to the maximum of the gain curve, because these two random media do not show resonant transport, in agreement with Mie theory. From Fig. 2a, instead, we observe a controlled overall shift of the lasing wavelength of ~35 nm between different photonic glasses. Furthermore, the random laser with $d = 0.9$ μm (green line) lases very far from the maximum of the dye florescence, which corresponds to the minimum gain length. The lasing wavelength dependence on the sample transmission is shown in Fig. 2c,d. Here the emission intensity is compared with the total transmission, for samples with $d = 0.9$ μm and $d = 1.0$ μm. The minimum in the transmission corresponds to a maximum in scattering strength, which tends to attract the lasing curve, pulling it towards lower wavelengths within the gain curve of the dye. Note that in this range the gain decreases with decreasing wavelength, which puts a limit on the wavelength shift induced by the scattering resonance. The shift in the central laser wavelength is, however, still as large as 35 nm for a difference in diameter of less than 10%.

In previous work[9,27], spheres or particles have always been dispersed in a solvent plus laser dye, making the refractive index contrast very low. This meant that at the given values of polydispersity it was impossible to resolve any Mie resonances. To confirm that indeed the transport resonances determine the lasing wavelength, we dispersed the spheres of the photonic glass in ethanol (sphere concentration 5 vol%). By doing so, we decreased the refractive index contrast and, as expected, the Mie resonances were washed out. The results are plotted in Fig. 3a. The dotted black line represents the photonic glass transmission, and the dotted red line the sphere suspension in ethanol, both with $d = 1.22$ μm. One can clearly see that the resonances are strongly damped. The corresponding emission spectra are plotted in Fig. 3b, where the colours represent the same sphere diameters as in the samples of Fig. 2a. Clearly, the resonant effect on the laser spectra is also strongly suppressed.

The richness of these resonant random systems can be further explored if one involves more than one Mie resonance in the lasing process. This can be achieved in two ways. The first is to use large spheres ($d > 2.0$ μm), which sustain very sharp resonances in the visible region if they are extremely monodisperse. Unfortunately, even the very small polydispersity of 3% for a glass with, for instance, $d = 3.0$ μm is enough to smooth out these narrow resonances (see Supplementary Information, Fig. S2). The second option is to broaden the gain curve of the active medium by combining two laser dyes. We prepared such a material by synthesizing a photonic glass and

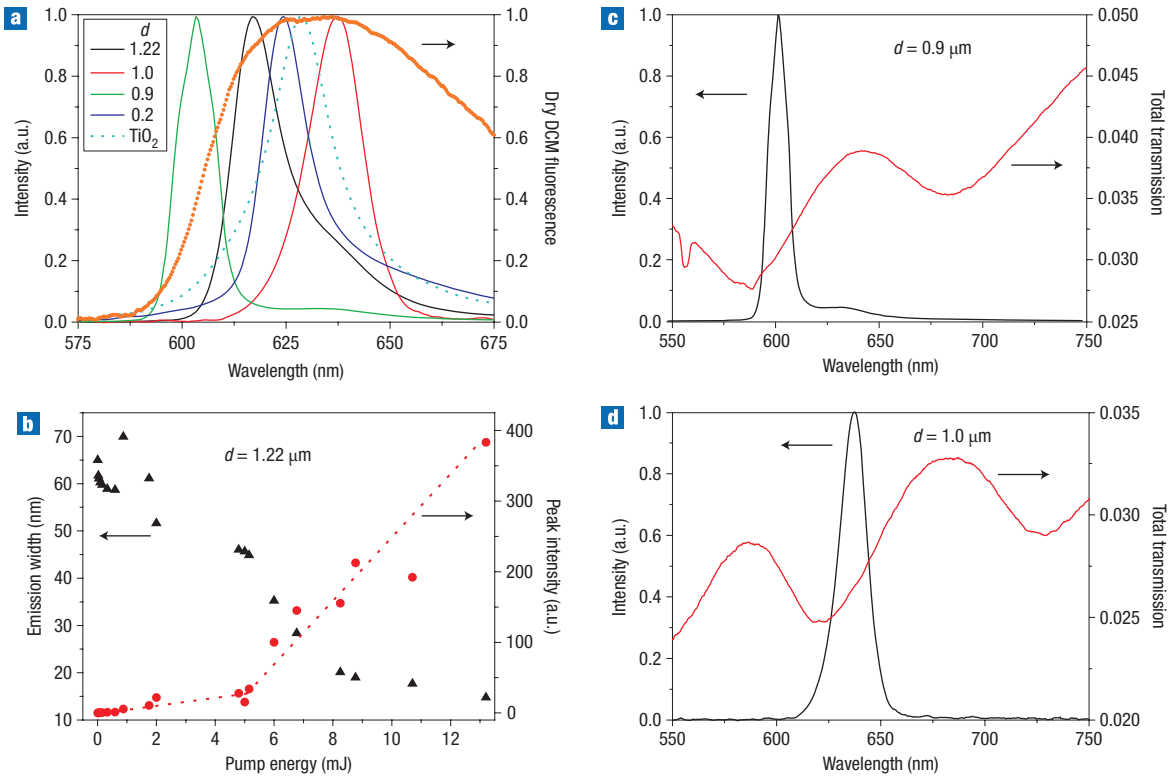

Figure 2 Random lasing action of photonic glasses. a, Random laser emission for photonic glasses with different sphere diameters compared with the pure dry-dye fluorescence (indicated by the arrow) and a reference sample made with TiO_2 powder doped with dry DCM (dotted cyan curve). The pump energy for all samples is ~14 mJ. **b**, Characteristic plot for the random laser ($d = 1.22$ μm), which highlights the threshold around 5 mJ of pump energy. **c**,**d**, Emission intensity and total transmission for photonic glasses with $d = 0.9$ μm and 1.0 μm, respectively. Lasing occurs close to the transmission minimum.

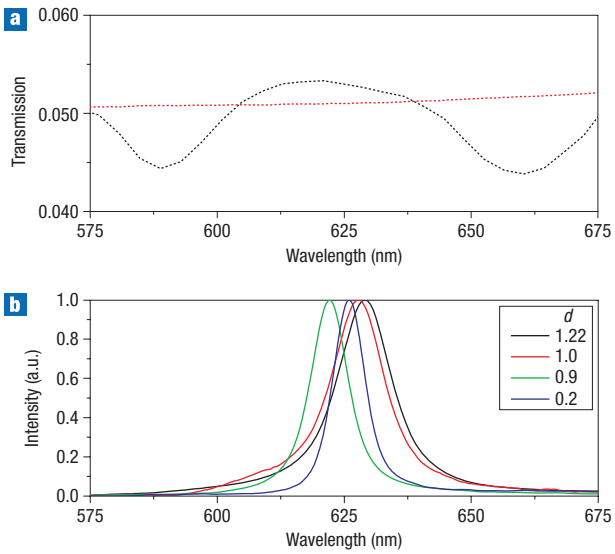

Figure 3 Random lasing action of sphere suspensions. a, Total integrated transmission for photonic glass (dotted black) and spheres suspension in ethanol (dotted red) with $d = 1.22$ μm and 5 vol% of concentration. The refractive index of the host medium increases from 1 (air) to 1.36 (ethanol). **b**, Random laser emission for different sphere suspensions in ethanol with DCM as the optical active medium, with an external pump energy fixed at 14 mJ. In this case the total spectral separation of the emission maxima for the different suspensions is only 7 nm.

incorporating dry DCM (as before) and a commercial dye Firefli™ encapsulated into small (~20 nm) polymer particles (1 wt%) that did not introduce additional resonances, but only shifted them by few nanometres because of the slight change of the filling fraction (not shown here). Typical emission spectra of these samples are plotted in the inset in Fig. 4, which shows the emission for two different pump powers, below (cyan) and above (orange) the lasing threshold. Two lasing peaks can be identified in this case, one around 610 nm and the other at 650 nm. In the main panel the ratio between the two lasing peaks is plotted versus excitation energy to illustrate mode competition. The cyan/orange curve in the inset corresponds to the cyan/orange experimental points in the main panel. The sample was made of spheres of diameter $d = 1.22$ μm and the corresponding transmission spectrum is the black curve of Fig. 3a. The two peaks nearly correspond with the transmission minima, and the emission dip corresponds to the transmission maximum. This indicates that we have involved two Mie resonances in the lasing process. Note that one has to exclude the possibility that other effects related to the dye mixture, for example, due to repumping, are not the cause of the observed double peak. To that end, we have performed measurements on a reference sample, with spheres of diameter 3 μm (without Mie resonances), where the two dyes were used in exactly the same way. We indeed do not observe any double peak emission (see Supplementary Information, Fig. S2).

In the experiments reported in this paper, we have presented random laser action from a three-dimensional system with resonant transport features. Our experiments demonstrate that Mie resonances can strongly effect random lasing and determine

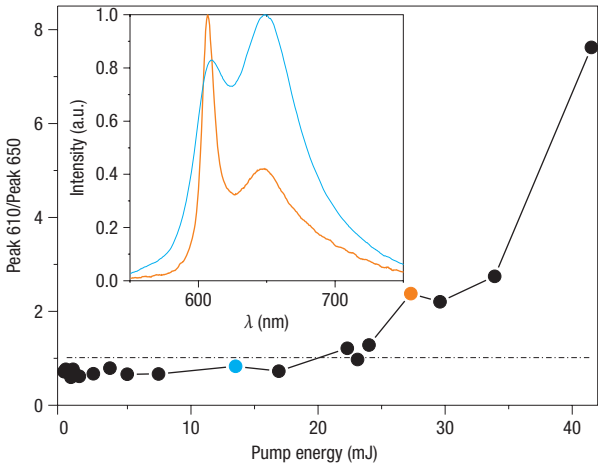

Figure 4 Mode competition between Mie resonances. Intensity ratio for the two lasing peaks of a photonic glass ($d = 1.22$ μm) doped with two laser dyes. The highest energy peak starts to dominate above threshold (20 mJ), reaching a value eight times larger than the low-energy one. The inset shows the emission spectra below (blue) and above (orange) threshold.

the lasing curve for photonic glasses. It is possible, this way, to select specific modes of the random laser and study mode-coupling mechanisms. In the experiments the laser dye was always distributed on the surface of the spheres. The random laser action could be even more pronounced and the lasing threshold lower if the dye was placed inside the spheres, close to the maximum of the resonant internal mode. This work shows that it is possible to control spectrally both light diffusion and random lasing emission, opening a novel route to active disorder based photonic devices.

METHODS

Polystyrene spheres were synthesized by free emulsion polymerization[28] with different diameters (0.2, 0.9, 1.0 and 1.2 μm) with a polydispersity around 2% measured with transmission electron microscopy. The surface potential of the polystyrene spheres ($d = 1.2$ μm) was −39.8 mV, established from a measurement of their electrophoretic mobility. In order to provoke the flocculation of the colloidal suspension, a 1 per cent volume of 0.01 M aqueous suspension of $CaCl_2$ or HCl had to be added to the initial polymeric colloidal suspension. The total solution was stirred under ultrasound for 5 min to force the flocculation of the spheres. To grow the photonic glass in a clean microscope glass slide previously hydrophilized, a volume of the charged colloidal suspension with a concentration 2 vol% was confined in a circular area (typically 1 cm radius) by applying adhesive tape of known thickness (millimetres). The system was kept at 50 °C for 3 h to evaporate the water. The filling fraction of the samples could be estimated as 0.55 by precisely weighting different samples with very well known geometry.

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