ABSTRACT: Total internal reflection is one of the most important phenomena when a propagated wave strikes a medium boundary, which possesses a wide range of applications spanning from optical communication to a fluorescence microscope. It has also been widely used to demonstrate conventional laser actions with resonant cavities. Recently, cavity-free stimulated emission of radiation has attracted great attention in disordered media because of several exciting physical phenomena, ranging from Anderson localization of light to speckle-free imaging. However, unlike conventional laser systems, the total internal reflection has never been implemented in the study of laser actions derived from randomly distributed media. Herein, we demonstrate an ultra-low threshold cavity-free laser system using air bubbles as scattering centers in which the total internal reflection from the surface of air bubbles can greatly reduce the leakage of the scattered beam energy and then enhance light amplification within a coherent closed loop. Our approach provides an excellent alternative for the manipulation of optical energy flow to achieve ultra-low threshold cavity-free laser systems, which should be very useful for the development of high performance optoelectronic devices.

INTRODUCTION

The random multiple scattering of light is a ubiquitous phenomenon in nature, for instance, the clouds, sugar, and salt become transparent if only single scattering happens. The interference effect among the multiple scattering in a disorder medium, which may result in an enhanced backscattering and localization of light, has received intense interest. As compared with the localization of electrons, the localization of photons provides a unique and fascinating phenomenon, which can induce laser actions without conventional cavity such as Fabry–Perot resonance. The resonators of conventional laser devices have to be designed precisely and arduously, while for a cavity-free lasing system, it possesses two amazing features simultaneously, namely, laser-level intensity and angle-free emission, which are mutually exclusive in incandescent bulbs, light-emitting diodes (LEDs), and conventional lasers. Such advantages of a cavity-free laser system, which enable to provide a promising high value of practical uses, especially for the high-lumen laser illuminations, speckle-free laser imaging, and even full-color laser displays, have attracted considerable attention and great efforts in academic research. In cavity-free systems, two basic elements, gain mediums to provide light emission through stimulated emission and appropriate random scatterers to induce the coherent feedback of light because multiple scattering are necessary to generate low spatial coherent emission. Light from the gain medium will experience the multiple scattering by the random scatterers, and the total gain will keep increasing to reach a threshold and then lead to the laser action when the total gain is larger than the loss. Thus, the novel design to demonstrate cavity-free laser actions tends to have the random scatterers with an appropriate mean free path similar to the wavelength of the emitted light, and the optical loss in the scatter process has to be low enough. Even though an intensive effort has been devoted to the research along this guideline with great success, to reduce power consumption for the generation of the laser action is still desired in order to meet the development of our sustainable planet. In this work, an alternative approach to circumvent the above rigid requirements and achieve an ultra-low threshold laser action assisted by a new paradigm with the total internal reflection derived from air bubbles as scattering centers is proposed and demonstrated.

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Air bubbles are naturally formed and seen in multiple places in everyday life. It is a result of several kinds of physical phenomena such as spontaneous nucleation of gas molecules under liquid, wave breaking, the impact of liquid drops to another liquid, and even changes in the solubility of air in water. In the course of history, air bubbles have been studied in many different ways. It has been utilized in several practical applications, for instance, ultrasound imaging for medical treatment, thermal inkjet printing, ultrasonic cleaning, and other microfluidics applications. 26 In addition, air bubbles are widely used in chemical and metallurgic engineering. 27 It is well known that illuminated light in an air bubble will experience a total internal reflection because of its low refractive index. Thus, the fact that the reflection occurs with a negligible loss of optical energy flow is possible. As the reflection of photon beam nowadays has multiple practical applications, such as solid state lighting, the design of a laser device by such a reflection process might lead to a significant reduction of the lasing threshold because of low energy loss. In addition, because of the structural simplicity and material usage, such devices can greatly reduce the cost of constituent materials. Moreover, the realization of a laser utilizing air bubbles as scattering centers would be very useful to reduce the waste and toxicity of the device in which micro/nano-particles are generally used as the scattering centers for light amplification. Thus, our unique strategy will serve as an excellent alternative for realizing the development of high performance optoelectronic devices with a wide range of applications.

The size-dependent band gaps and high quantum yield of colloidal semiconductor quantum dots (QDs) have great potential for a wide spectrum of optical applications such as QD-based LEDs, solid-state lighting, lasers, and biotechnology. 28–32 Especially, a sequence of red, green, and blue (RGB) monochromatic CdSe/ZnS core–shell QDs spanning over the visible spectrum have been demonstrated. To illustrate our proposed working principle, here, we implement CdSe/ZnS core–shell QDs as the optical gain media to integrate with air bubble-based total-reflective scatterers for the demonstration of color-tunable and ultra-low threshold cavity-free lasing systems. To confirm the important role of air bubbles in the cavity-free laser action, we have performed experiments under different temperature treatments to fine-tune the density of air bubbles, which in turn alters the formation of the scattering environment and the properties of the laser action. We believe that the prototype proved here can push the boundary of laser research via this unprecedented scattering system as well as through novel applications.

## RESULTS AND DISCUSSION

**Air Bubble-Based Devices Design and Fabrication.** The schematic illustration of the multiple scattering in our device is shown in Figure 1a. In order to fabricate the device, an aqueous solution of polyvinyl alcohol (PVA) was prepared, and an appropriate amount of baking soda (NaHCO3) was dissolved in the solution. Then, an aqueous solution of semiconductor QDs, for example, CdSe/ZnS core–shell QDs in water was added into the solution and stirred until a uniform solution was achieved. The mixed solution was then drop casted on a SiO2 substrate and heated at 90 °C for 5 min. Because of the heating effect, the NaHCO3 is decomposed, and CO2 and H2O are produced, followed the chemical reaction 2NaHCO3 → Na2CO3 + H2O + CO2. The produced CO2 can assist the formation of air bubbles in the drop casted film during the drying process of the mixed solution. The as-grown film then consists of semiconductor QDs as well as air bubbles embedded in the polymer film. By changing the weight fraction of the NaHCO3, the heating temperature, and heating time, the bubble size and bubble density can be controlled. The scanning electron microscopy (SEM) image of the air bubbles produced by this method is shown in Figure 1b. The mean radius of the bubbles is about 1 μm, and the distances between bubbles are several hundred nanometers. Interestingly, with an appropriate design of the bubble size and its spatial
distribution, the air bubbles are suitable to induce multiple scattering of the photons traveling in the sample for the formation of coherent closed loops, while the embedded QDs in the polymer matrix can serve as an optical gain medium. For comparison, the QDs/PVA film without NaHCO₃ was heated at 90 °C for 5 min on the SiO₂ substrate, and there is no obvious bubble in the SEM image of this sample, as shown in Figure 1c. This outcome proves the effect of NaHCO₃ to generate air bubbles. Note that, no pronounced peaks are observed in the photoluminescence (PL) spectra of this sample without the assistance of air bubbles, as shown in Figure 1d.

**Ultra-Low Threshold Cavity-Free Laser Assisted by Air Bubble-Based Devices.** The emission spectra from the as-grown polymer film consisting of air bubbles and CdSe/ZnS core–shell QDs of emission centered around ~630 nm under a 374 nm pulsed laser of a pulsed width (20 ps) is shown in Figure 2a. Quite interestingly, the emission spectra show a drastic change depending upon the fluence of the pumping laser. Clearly, after a threshold power (~35 μJ cm⁻²), pronounced sharp peaks appear in the emission spectra. In order to unveil the origin of the sharp peaks, we have plotted the integrated emission intensity as a function of pumping energy density, as shown in Figure 2b, which exhibits pronounced threshold behavior. In the same way, the full width at half maxima (fwhm) of the emission line also shows a sublinear change with a similar threshold behavior at a pump fluence of 35 μJ cm⁻². The abovementioned phenomena can be interpreted as a clear signature of attaining laser actions in the system. Under the excitation of a pumping laser, the emitted light from the QDs suffers from multiple scattering processes owing to the existence of the air bubbles in the matrix. For a relatively dilute collection of spheres of number density, the optical mean free path l can be approximated as 

\[
l \sim \frac{2a}{\sqrt{3f}}
\]

where \(a\) is the radius, and \(f\) is the volume filling fraction of the sphere.³² By this method, the mean free path of the bubble system is approximated about 500 nm, which fits well with the wavelength to produce a coherent feedback for the emitted photons arising from QDs to attain visible light laser actions.¹⁹ The laser action occurs when the optical gain overcomes the total energy loss owing to the existence of feedback loops because of scattering processes. Importantly, the refractive index of the air bubble is 1, which is the lowest among all the materials for producing the multiple scattering to achieve amplification. This unique feature enables that air bubbles can induce the total internal reflection when the emitted light arises from the QDs embedded inside the polymer matrix. The schematic diagram of the total internal reflection is shown in Figure 2c. When the incident angle of light is larger than 42.5°, the total internal reflection will occur with almost zero energy loss during the scattering process. When the incident angle is smaller than the critical angle, light refracted into the bubbles will be refracted out of the bubbles again, which can also generate scattering and have a large optical loss similar to previously published reports. Therefore, the lasing action can be more easily achieved, and the lasing threshold can be greatly reduced. To further consolidate our observations of the laser action, the time-resolved PL (TRPL) measurements and the angle-dependent measurements have been performed. The outcome of the TRPL measurements for the sample is shown in Figure 2d. The carrier lifetime has a sublinear change as a function of pumping intensity because the emission process turns to the stimulated emission with the increase of pumping energy density. The emission spectra as a function of a sample-detector angle of the sample is shown in Figure 2e. The sublinear change of lifetime and the property of angle dependence provide clear evidence for the occurrence of random laser actions.
Demonstration of Cavity-Free Laser Spanning over the Visible Spectrum. We have designed the PVA–air-bubbles–QDs composite devices with a set of commercially available RGB CdSe/ZnS core–shell QDs spanning over the visible spectrum to construct a wide spectrum lasing system. Similar to the red light cavity-free laser as mentioned above, under the excitation of a 374 nm laser illumination, the spectra of the blue and green light cavity-free laser actions are shown in Figure 3a,b. When pumping energy density is gradually increased, multiple pronounced sharp peaks of linewidth < 0.5 nm are superimposed on the PL spectra. The integrated intensity and spectral linewidth fwhm for blue and green color as a function of pumping energy density are shown in Figure 3c,d. Quite interestingly, the threshold pumping energy density of the laser, based on such colloidal CdSe/ZnS core–shell QDs of different emission wavelengths as the gain media, can
be as low as ~20 μJ cm⁻². To the best of our knowledge, it is the lowest threshold pumping energy density ever reported among all random lasing systems based on the colloidal QDs as the gain media. 34-38 The low threshold value is a result of the formation of coherent closed loops because of multiple scatterings in which the total internal reflection of the emitted light results in almost no energy loss during the multiple scattering processes.

**Changing of Air Bubble Density to Tune Cavity-Free Laser.** To figure out the suitable condition of the fabrication of air bubbles for the observed laser action, herein, we show that by changing the air bubble density, it can lead to the different distances between air bubbles and induce the different mean free path for the emitted photons. Heating temperature can easily influence the bubble density of the system. This is because that air bubbles are generated because of the decomposition of NaHCO₃ when the formation of the film is under heating treatment. It is known that the thermal decomposition of NaHCO₃ starts at about 50 °C. 39 We have fabricated the samples with different heating temperatures at 30, 60, and 90 °C. It was found that the composite film produced at a heating temperature of 30 °C will not generate air bubbles in the film, and air bubbles start to appear at 60 °C. The thermal decomposition at 90 °C is much stronger, and it produces air bubbles with higher density. The corresponding SEM images of the devices under three heating conditions are shown in Figure 4a–c, which show a systematic change in bubble density as a function of the baking temperature. The emission spectra of the samples with different color light-emitting QDs can be tuned by the heating temperature at constant pumping power density, as shown in Figure 4d–f. Interestingly, as no air bubbles are produced in the sample under 30 °C treatment, no lasing peaks are observed. Under 60 °C treatment, the air bubbles start to nucleate, but the density of the bubbles are not enough for forming a good coherent closed loop to provide enough optical feedback for the emitted light. Under 90 °C treatment, high density of air bubbles are filled in the film in which a strong optical feedback to the emission can be provided, and the prominent appearance of the lasing peaks is observed. Note that as heating treatment is higher than 90 °C, it will make the PVA film very fragile, and the formation of the PVA film becomes difficult. Thus, we limit heating treatment temperature below 90 °C.

**CONCLUSIONS**

Based upon the above studies, we have successfully demonstrated ultra-low threshold cavity-free laser devices with a wide visible spectrum assisted by air bubbles. The air bubbles produced by a cost-effective method can serve as excellent scattering centers, which enable a strong scattering of the emitted photons from the QDs with low energy loss to achieve the stimulated emission of radiation because of the total internal reflection induced by the smallest refractive index. Thus, our approach is not only very cost-effective with commercially available materials but also holds a new paradigm for low threshold cavity-free lasing devices by reducing energy loss through the total internal reflection, rather than traditional methods of improving the morphology of the resonators.

**EXPERIMENTAL SECTION**

**Device Fabrication.** To prepare the PVA solution, we dissolved the solid PVA grains into deionized water with a mass fraction of 4 wt % and then stirred it for 30 min at room temperature. The NaHCO₃ was dissolved into the PVA solution with a concentration of 50 mg/mL. The CdSeS/ZnS core–shell QDs of emission centered at 465 nm (blue), 545 nm (green), and 635 nm (red) were purchased from Sigma-Aldrich. The ZnO and the TiO₂ are mixed with the PVA solution with a concentration of 10 mg/mL.

**Instrument of Measurement.** The PL measurements were performed by a pulse diode laser (PicoQuant, PDL 800-B, a center wavelength of 374 nm, 70 ps, 2.5 MHz) through the lens to focus with a 5 μm² spot size at 90° incident angle using a HORIBA Jobin Yvon TRIAX 320 spectrometer to collect the signals. The lasing spectrum and carrier lifetime were measured by a HORIBA Jobin Yvon TRIAX 320 spectrometer in which 374 nm pulsed laser was used as the pumping source. The SEM images were measured by a JEOL JSM-6500F field-emission scanning electron microscope under the acceleration voltage of 7 kV, working distance of 7.8 nm, and x11,000. Before measuring, a thin gold layer on the sample was sputtered by using a fine gold coater (EMI TECH KSS 0X) for 1 min under 5 mA applied current to avoid the charging effect.

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**Author Contributions**

H.-W.H., G.H., and Y.-F.C. supervised the project and conceived the study. H.-W.H., G.H., and Y.-M.L. were involved in the discussion of mechanisms. The experiment was designed through contributions of all authors. The manuscript was written by H.-W.H., G.H., and Y.-F.C. All authors have given approval to the final version of the manuscript.

**Notes**

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