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Random Lasing Action from Randomly Assembled ZnS Nanosheets

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Abstract Lasing characteristics of randomly assembled ZnS nanosheets are studied at room temperature. Under 266-nm optical excitation, sharp lasing peaks emitted at around 332 nm with a linewidth less than 0.4 nm are observed in all directions. In addition, the dependence of lasing threshold intensity with the excitation area is shown in good agreement with the random laser theory. Hence, it is verified that the lasing characteristics of randomly assembled ZnS nanosheets are attributed to coherent random lasing action.

Keywords ZnS nanosheets · Random lasing · Ultraviolet

As an important functional material for electronics and optoelectronics, zinc sulfide (ZnS) was one of the first semiconductor materials discovered few decades ago. It has a wide band gap of 3.7 eV at room temperature [1], which is a key material for sensors [2], flat panel displays [3], ultraviolet light emitting diodes [4], and lasers [5]. Recently, the synthesis and characterization of 1D ZnS nanomaterials and nanostructures has been of growing interest owing to their promising application in nanoscale optoelectronic devices [6, 7]. Optical wave confinement and lasing emission have been reported in individual ZnS nanoribbons and nanowires [8, 9]. In this paper, the optical properties of randomly assembled ZnS nanosheets are investigated. It is observed that the ZnS samples exhibit an intense random lasing emission with coherent optical feedback, which suggests a possibility of achieving random laser action in randomly assembled ZnS nanosheets.

A layer of 2-μm-thick randomly assembled ZnS nanosheets were deposited on a Si substrate by a vapor transport method inside a horizontal tube furnace [10]. Detailed fabrication procedures been described elsewhere [11]. Figure 1a shows the XRD pattern of the as-grown sample, which XRD peaks are related to the hexagonal wurtzite (WZ) ZnS structure. The diffraction pattern matches well to a hexagonal ZnS (JCPDS No. 80-0007, vertical bars). The field emission scanning electron microscopy (FESEM) image of the randomly assembled ZnS nanosheets was shown in Fig. 1b. It is shown that most of the as-growth products have a sheet-shaped morphology with a typical length of 5 to 10 μm, an average width of about 400 nm and an average thickness of about 20 nm. Figure 1c shows the transmission electron microscopy (TEM) image of a single nanosheet, which reveals that the nanosheet has a sharp edge. High-resolution TEM image and diffraction pattern are shown in Fig. 1d, which illustrates that the nanosheet is composed of single-crystalline-ZnS structure.

The sample were optically excited by a frequency-quadruplet 266 nm pulsed Nd:YAG laser with 120 ps pulsewidth and 10 Hz repetition rate. A spherical lens was used to focus a pump beam of $\sim$1 mm in diameter onto this sample's surface. Emission was collected in the direction perpendicular to the surface of the sample. Emission spectra of the sample were analyzed by an Oriel MS257 monochromator (spectral resolution of $\sim$0.1 nm) attached with a photo-multiplier tube. As shown in Fig. 2, when the pumping intensity reached a pump threshold, P_{th}, a shape peak with linewidth of $\sim$0.4 nm emerged from the single-broad emission spectra at 332 nm. For the pump intensity

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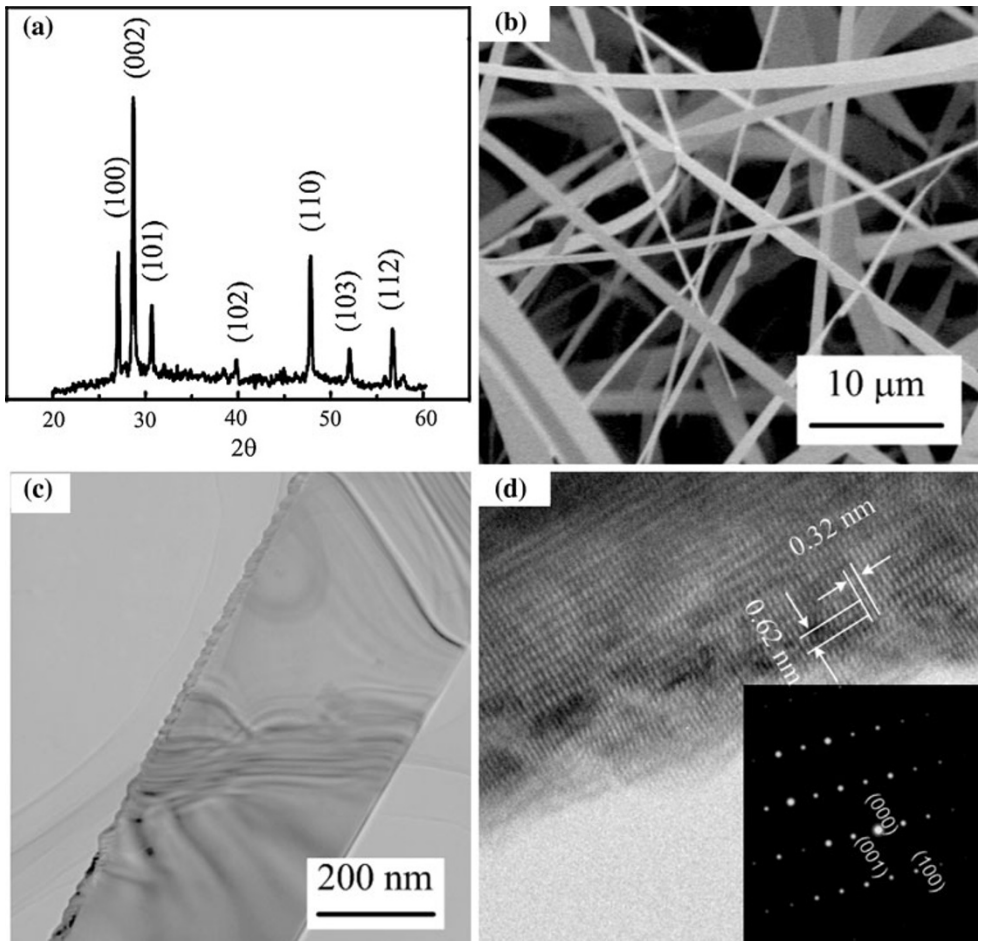

Fig. 1 **a** XRD pattern and, **b** FESEM image of the randomly assembled ZnS nanosheets. **c** TEM image and, **d** high-resolution TEM image of a single ZnS nanosheet, the insert shows the corresponding diffraction pattern

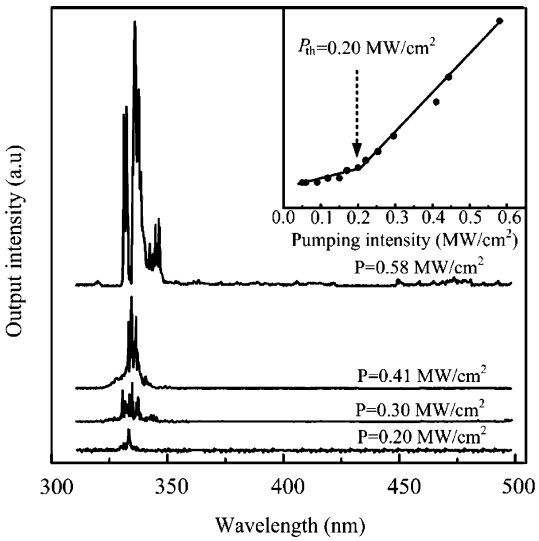

Fig. 2 Emission spectra of the randomly assembled ZnS nanosheets under the excitation of 266-nm optical pumping. The *insert diagram* shows the corresponding light–light curve of the ZnS sample

further increase, more peaks are excited from the emission spectrum. The emission peaks are related to the band-to-band radiative recombination at the ZnS nanosheets. On the other hand, no visible peak due to defect related radiative recombination center is observed from the emission spectra. The insert of Fig. 2 plots the emission intensity of the ZnS nanosheets versus pump intensities (i.e., light–light curve of the ZnS nanosheets). It is noted that the corresponding light–light curves exhibit a kink at pump intensity of $\sim$0.2 MW/cm^2, which is equal to the pump threshold, P_{th}. Hence, these verified that the randomly assembled ZnS nanosheets demonstrated lasing emission at wavelength $\sim$332 nm.

Figure 3 shows the emission spectra under $\sim$0.3 MW/cm^2 pumping intensity of the ZnS nanosheets with different observation angles, θ. It is noted that the emission spectra are different at different value of θ. This is because closed-loop random cavities formed by multiple scattering inside the randomly assembled ZnS nanosheets can emit at different directions. In addition, it is observed that the number of lasing peaks (i.e., random modes) increases with the reduction of θ. This is because the scattered light is partially trapped between the top and bottom surfaces of the randomly assembled ZnS nanosheets film. Light scattered from the ZnS nanosheets to the bottom surface of the film will be partially reflected back to the film by the flat surface

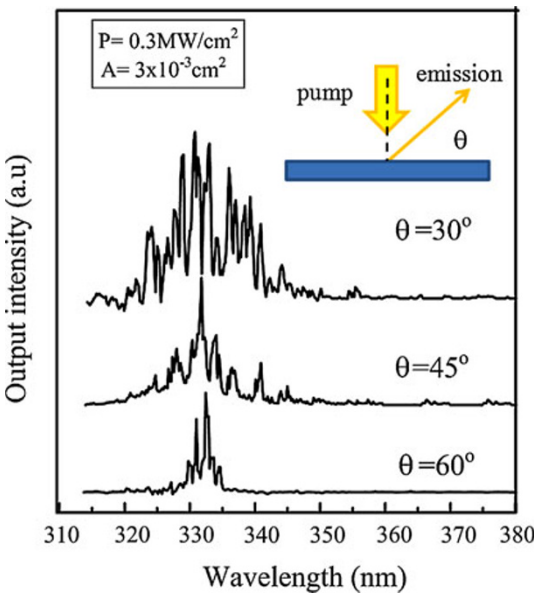

Fig. 3 Emission spectra of the randomly assembled ZnS nanosheets detected at different observation angle, θ

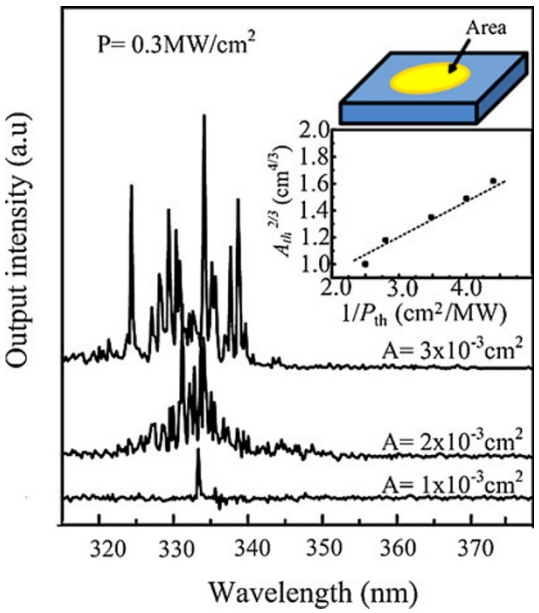

Fig. 4 Emission spectra versus different excitation areas, A. The *insert* shows the relation between $A_{\text{th}}^{2/3}$ and P_{th}^{-1} of the randomly assembled ZnS nanosheets

of Si substrate. On the other hand, light scattered to the top surface of the film may experience a reduction in effective refractive index so that light will also be partially reflected back to the film. As a result, strong random lasing action (i.e., more random modes can be excited) is obtained at small value of θ due to the transverse optical confinement of the film.

The dependence of excitation area on the lasing spectrum was also studied. Figure 4 shows the variation of emission spectra for the excitation area, A, varies from 1×10^{-3} to 3×10^{-3} cm^2 at a constant pump intensity of 0.3 MW/cm^2. It is observed that before a critical area, A_{th} (i.e., $\sim 1 \times 10^{-3}$ cm^2) is reached, no sharp lasing peak is observed. However, when the excitation area exceeds A_{th}, sharp lasing peaks with a linewidth of less than 0.4 nm appear. The number of sharp lasing peaks increases with the increase in A. The relation of A_{th} with P_{th} is plotted in the insert of Fig. 4. The value of P_{th} was estimated by searching for the position of kink in the light–light curve for a constant value of A. The error in measuring P_{th} is limited to 0.025 MW/cm^2 as this is the excitation interval of the pumping source. It is found that $A_{\text{th}}^{2/3}$ is roughly proportional to P_{th}^{-1}. In this case, the randomly assembled ZnS nanosheets film should behave like a quasi-3D random medium (i.e., a 3D random medium with transverse optical confinement of scattering light along the random medium), so that the relationship $A_{\text{th}}^{2/3} \sim P_{\text{th}}^{-1}$ is satisfied [12]. On the other hand, if the transverse optical confinement (film thickness) is strong (compatible with lasing wavelength), the film should be considered as a 2D random medium with a relationship $A_{\text{th}}^{1/2} \sim P_{\text{th}}^{-1}$ [13]. Hence, all these lasing properties detected from the randomly assembled ZnS nanosheets sample agree with the coherent random laser theory [14, 15].

As the lasing mechanism of the ZnS/ZnS biaxial nanosheet is due to coherent random laser action, it is also possible to deduce the cavity length of the corresponding closed-loop cavity modes by Fourier transform (FT). Figure 5a plots the FT of the lasing spectra of the randomly assembled ZnS nanosheets under optical excitation at 0.58, 0.41, and 0.2 MW/cm^2. A series of broad peaks of harmonics, which corresponding to different cavity length of the random modes, are observed from the FT patterns. The corresponding closed-loop path length, L, of the fundamental cavity modes at different optical excitations are found to be ~ 15, ~ 7, and ~ 3 μm, respectively. As shown in Fig. 5b, it is expected that under larger excitation intensity, the randomly assembled ZnS nanosheets can get higher optical gain. Therefore, more closed-loop paths for light can be formed. In this case, random laser action could occur in more cavities formed by recurrent scattering. Hence, it is required to increase the value of L in order to allow more closed-loop random cavities to be formed [10, 14].

In our previous studies of randomly assembled SnO_2 nanowires, which have similar morphology to that of the ZnS nanosheets, ultraviolet random lasing action was observed under optical excitation. [15] Hence, this implies that random media can be easily realized from the nanostructured films with similar morphology despite their difference in radiative recombination mechanism. This is because the radiative recombination mechanism of ZnS is

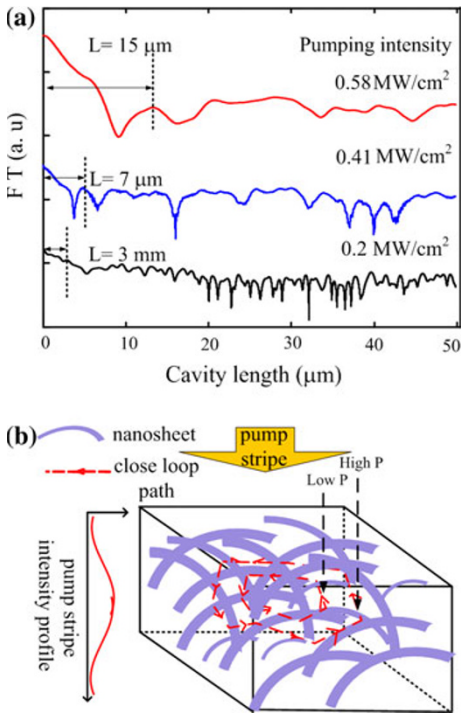

Fig. 5 **a** FT patterns of the randomly assembled ZnS nanosheets with different pumping intensity. The arrow indicates the cavity length, *L*, of the fundamental closed-loop cavity modes. **b** A schematic diagram shows the formation of closed-loop path of light obtained from recurrent light scattering under different excitation intensity

completely different to that of SnO_2. ZnS (SnO_2) is mainly related to direct bandgap (surface defect-state) recombination. In conclusion, ultraviolet lasing is observed from randomly assembled ZnS nanosheets at room temperature. Lasing wavelength and threshold are found to be about 332 nm and 0.2 MW/cm^2, respectively. Furthermore, the dependence of threshold pump intensity on the excitation area agrees well with the random laser theory. Hence, it is verified that the lasing mechanism of randomly assembled ZnS nanosheets is due to coherent random lasing action.

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