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Random lasing from dye-Ag nanoparticles in polymer films: Improved lasing performance by localized surface plasmon resonance

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ABSTRACT

Random multimode lasers are achieved in 4(dicyanomethy-lene)–2- tert-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)4H-pyran (DCJTB) doped Polystrene (PS) thin films by introducing silver nanoparticles (Ag NPs) as scatterers. Ag NPs were prepared by polymer protection method. By optimizing the concentration of reactant of $AgNO_3$ and the ratio of Ag NPs to DCJTB, the devices emit a resonance multimode peak at a center wavelength of 625 nm and the threshold excitation intensity is as low as 0.0031 mJ/pulse. It can be seen that the microscopic random resonance cavities can be formed by multiple scattering of Ag NPs which supply the localized surface-plasmon resonance (LSPR) coupling with the lasing emission to enhance the lasing efficiency. Our results demonstrate that Ag NPs are promising candidate as alternative sources of coherent light emission to realize low-threshold organic random lasers.

1. Introduction

Surface plasmons (SPs) are surface charge density oscillations that exist at a metal/dielectric interface. These oscillations, excited by the interaction between light and metal surfaces [1], are known to increase the density of states and the spontaneous emission rate in the semiconductor [2–4] and lead to the enhancement of light emission. They have been extensively used in various applications, such as surface enhanced Raman [5], organic light-emitting diodes (OLEDs) [6], and biosensors. In recent years, the coupling between a SPs and an optically active medium became a hot topic. For example, Noginov et al. [7] provide a major step forward for plasmon-based nanolasers based on a gold core centered in a dye-doped silica shell, where the optical gain is supplied by organic dye molecules embedded in the silica shells and the surface plasmons are provided by the gold cores. In addition, the metallic NPs with periodic arrangement can act as a grating and lead to distributed feedback lasers [8,9]; gold or silver NPs with random distribution were also found to lead to the random lasing by the effects of enhanced localized EM fields and scattering [10–13].

Recently, particular interest has been drawn to the effect of noble metal nanoparticles on the random lasing characteristics [14,15]. In previous reports, the lasing threshold was reduced and its emission was greatly enhanced by the introduction of Ag or Au NPs [16,17]. Recent analysis has shown that a large fraction of light generated in a typical random laser is coupled into SP modes, especially in devices incorporating small molecules such as organic dye. Heydari et al. reported the emission enhancement in the plasmon assisted random laser by coupling between the dyes and the localized surface-plasmon resonance (LSPR) of Au NPs [17]. Dice et al. demonstrated incoherent random lasing from a suspension of Ag NPs in a methanol solution of Rh6G [18]. In these works, noble metal nanoparticles may strongly scatter and absorb visible light due to the LSPR. The electric field can be confined in the vicinity of the surface of metal NPs due to LSPR; as a consequence, such confinement can be very effective for the excitation of active centers to provide high optical gain for laser oscillation [13].

Recent studies show that the scattering properties of metal NPs are very sensitive to particle size and morphology [19]. In order to evaluate the effect of metallic particle size on random lasing of dyes, in this work, the optical pumped random lasing properties were usually investigated in presence of dye-Ag nanoparticles in polymer films. Ag NPs in different sizes were synthesized by the chemical reduction method and introduced into the gain media of the 4(dicyanomethy-lene) –2-tert–butyl –6(1,1,7,7–tetramethyljulolidyl-9-enyl)4H-pyran (DCJTB) doped polystrene (PS). The objective of this paper is to study the influence of the excited SPs from the Ag NPs with different sizes on the lasing properties. By optimizing the concentration of the reactant of $AgNO_3$, we found that surface-plasmon-enhanced lasing emission with reduced thresholds had been obtained.

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2. Experimental section

2.1. Synthesis of Ag nanoparticles

In our experiments, Ag NPs were prepared by polymer protection method. Here, polyvinylpyrrolidone (PVP), as protective agent, were added into the reactant silver nitrate ($AgNO_3$) solution (the molar ratio of PVP to $AgNO_3$ is 1:2). At the temperature of 60 °C, the mixed solution was fully stirred, and then 0.5 mol/L hydrazine hydrate ($N_2H_4{\cdot}H_2O$) solution as reducing agent was slowly added. The obtained Ag NPs were washed by alcohol, acetone, ultrapure water in turn, then dried in the room temperature. To determine the effect of the size of Ag NPs on lasing action, we prepared Ag NPs in different sizes by changing the molar concentration of $AgNO_3$ in $N_2H_4{\cdot}H_2O$. The concentrations of $AgNO_3$ in $N_2H_4{\cdot}H_2O$ were changed from 0.01 to 0.6 M, respectively.

2.2. Fabrication of Ag nanoparticles/organic dye random laser

DCJTB, as the gain media, was first dissolved in PS by using chloroform as solvent. The optimized weight ratio of DCJTB to PS was kept constant to 4% by weight. Then, Ag NPs, as scattering centers, were added into the DCJTB:PS blend. To avoid the cluster of the Ag NPs, the blend was ultrasounded 10 min and then spincoated onto the quarz substrate to form a Ag NPs dispersed DCJTB:PS film (Ag NPs @ DCJTB: PS). For comparison, a DCJTB:PS film without Ag NPs was also fabricated. Furthermore, to optimize the concentration of Ag NPs, four samples with different ratios of Ag NPs to DCJTB (1:0.5, 1:1, 1:2, and 1:4) were prepared.

2.3. Measurement of random lasing properties

The experimental set-up to investigate the laser action followed Ref. [20]. The pump source was a frequency tripled Nd-YAG laser (Spectra-Physics) delivering 2 ns pulses at 532 nm with a 10 Hz repetition rate. The output pulse energy of the pump laser was controlled using neutral density filters. An adjustable slit and a cylindrical lens were used before the beam splitter in order to shape the beam into a narrow stripe with a continuously varied length on the sample film. The films were pumped at normal incidence with the long axis of the pump beam perpendicular to the edge of the sample. The output signals were detected by fiber-coupled CCD spectrometer (JYSPEX CCD3000). The pumped energies from the laser were measured using a calibrated laser power and energy meter (Gentec). For comparison, the photoluminescence (PL) was also measured using a continuous wave (CW) 532 nm laser. The morphologies of the as-synthesized Ag NPs were characterized by a field emission scanning electron microscope (FE-SEM, TESCAN MARI3) and a transmission electron microscopy (TEM, Libra-200FE).

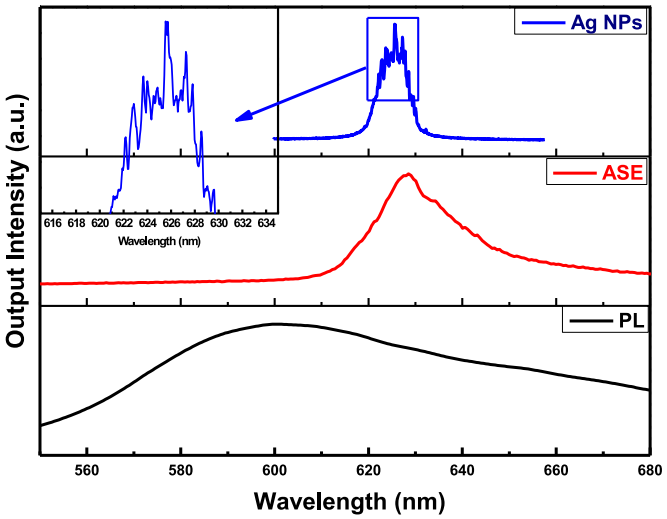

Fig. 2. Emission spectra of the neat DCJTB:PS film pumped by 532 nm constant laser (black curve) and 532 nm pulsed laser (red curve) and the emission spectrum of the Ag NPs @ DCJTB:PS film pumped by 532 nm pulsed laser (blue curve). The image shows a portion of the spectrum of the Ag NPs @ DCJTB:PS film under higher magnification. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3. Results and Discussions

Fig. 1a) shows the scanning electron microscopy (SEM) images of the Ag NPs, when the molar concentration of $AgNO_3$ is 0.01 M. It can be seen that a large number of Ag NPs have been successfully synthesized, and mostly in the shape of sphere and the average diameter is 30 nm, when the concentration of $AgNO_3$ is 0.01 M. With the concentration of $AgNO_3$ increasing, the particle size of Ag powder is gradually increased. When the molar concentration of $AgNO_3$ is 0.03 M, the transmission electron microscopy (TEM) image of Ag NPs were measured and shown in Fig. 1b). The average diameter Ag NPs is increased to 100 nm. The increase of $AgNO_3$ concentration leads to the acceleration of reduction reaction. The formation of the crystal nucleus increases at the beginning, and the trends of agglomeration are greater than the diffusion during the formation of the grains. Thus the size of Ag NPs gradually increased.

In order to reveal the role of Ag NPs in the DCJTB:PS film, we also prepared the neat DCJTB:PS film for comparison. The emission spectra from the neat DCJTB:PS film and the Ag NPs scattered DCJTB:PS film (the concentration of $AgNO_3$ is 0.03 M and the ratio of Ag NPs to DCJTB is 1:1 by weight) are shown in Fig. 2. The photoluminescence (PL) spectrum exhibits a broad peak at 600 nm, whereas the spectrum excited by 2 ns pulsed pumping is dramatically narrowed to a 19 nm half-width peak at 628 nm. The laser pulses create a significant

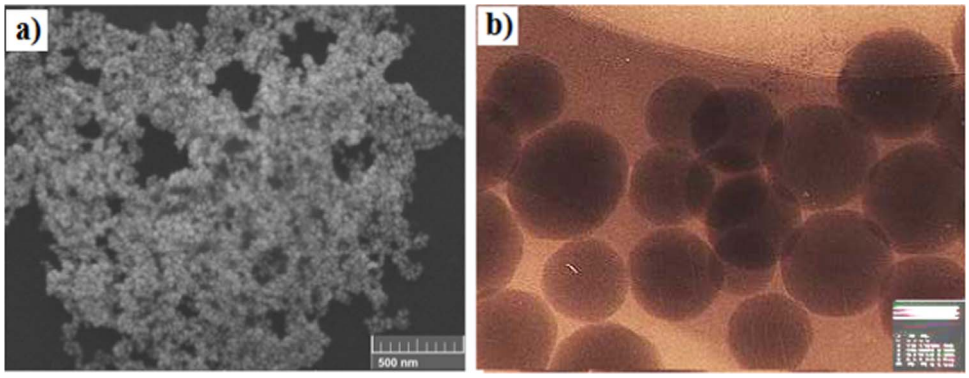

Fig. 1. a) The scanning electron microscopy (SEM) image of Ag NPs prepared by polymer protection method with the $AgNO_3$ concentration of 0.01 M; b) Transmission electron microscopy (TEM) image of the Ag NPs with the $AgNO_3$ concentration of 0.03 M.