Gold nanoparticle-enhanced amplified spontaneous emission of laser dye molecules in diode-pumped organic solid-state lasers

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Abstract. Gold nanoparticles (AuNPs) were introduced to enhance surface-amplified spontaneous emission of laser dye molecules, 4-(dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) doped N,N’-bis(1-naphthyl)-N,N’-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB), taking advantage of localized surface plasmonresonance (LSPR) effect and scattering effect. With emission received from the back surface of the substrate, the optically pumped gain medium with AuNPs, exhibits higher peak intensity, lower threshold, and better Q-factor of when compared with the neat gain medium without AuNPs. Moreover, to realize an organic solid-state laser pumped by electroluminescence emission in an integrated organic light emitting diode (OLED), NPB: DCJTB was embedded as color conversion-hole transport layer (CC-HTL). The AuNPs deposited on the ITO glass substrate of the OLED were also employed to enhance the photoluminescence of the CC-HTL. The maximum luminance, current efficiency and power efficiency improved by 21.55%, 21.90% and 42.11% at 150 mA/cm² of AuNPs-OLED, respectively, compared to the OLED without AuNPs. These results were attributed to the enhanced hole injection caused by AuNPs as well as LSPR and scattering effects. The introduction of AuNPs provides a simple and promising method to realize diode-pumped organic solid-state lasers.

1. Introduction
The metal nanoparticles (MNPs) have been widely used in designing low-threshold and high-quality organic lasing [1-3], particularly, MNPs can enhance the lasing efficiency via localized surface plasmon resonance (LSPR) effect and scattering effect [4,5]. Bergman and Stockman proposed the spacer (surface plasmon amplification by stimulated emission of radiation) effect [6-8]. However, these studies do not provide much attention to surface-emitting organic lasers (SOLs), which exhibits many advantages compared to edge-emitting lasers, such as easy to combine with optical fibers, convenient to test, densely packed and precisely arranged arrays [9,10]. The SOLs have been achieved up to now mostly in the vertical external-cavity SOLs (VECSOLs) [11,12] or distributed feedback SOLs (DFB-SOLs) [13], in which low and instability output power exits. To improve the SOLs, MNPs confining light in a much smaller volume (mode volume) than the above two structures, can result in a local enhancement of the electric field [14].
On the other hand, in the past decades, organic light-emitting diodes (OLEDs) have attracted intense academic and industrial interest, which results in the great progress of efficiency enhancement [15-17]. However, these research achievements have not been applied to the realization of organic semiconductor laser diodes. Many attempts to observe electrically pumped lasing in organic semiconductor cavities have been carried out but have not yet met with success since many obstacles exist to reach this goal [18-20]. In previous work, Wei et al proposed that organic thin films as color conversion-hole injection layers of OLEDs may ultimately enable electrically OLEDs-pumped lasers [21-23].

In this work, gold nanoparticles (AuNPs) were introduced to enhance the surface amplified spontaneous emission (ASE) of red laser dye molecules, namely, 4-(4-dicyanomethylene)-2-t-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyr (DCJTB) doped N,N’-bis-(1-naphthyl)-N,N’-diphenyl-1,1’-biphenyl-4,4’-diamine (NPB). When the NPB: DCJTB thin film with AuNPs was optically pumped from an oblique angle and the emission was received from the back surface of the substrate, higher peak intensity, lower threshold, and higher Q-factor of its ASE were achieved. Moreover, to realize an organic solid-state laser pumped by electroluminescence (EL) emission in integrated OLEDs, NPB: DCJTB was embedded as color conversion-hole transport layer (CC-HTL). The AuNPs deposited on the ITO glass substrate of the OLEDs were also employed to enhance the photoluminescence (PL) of the CC-HTL.

2. Experimental

Firstly, we investigated the thickness-dependent effect of AuNPs to the ASE of the optically-pumped organic thin films. Structures 0-4 with the structure of glass/AuNPs (x nm)/NPB (4 nm)/NPB: 2wt% DCJTB (100 nm) were fabricated, where x was set to be 0, 0.4, 0.8, 1.2, and 1.6, respectively. They were pumped by an Nd:YAG laser (FTSS 355-50, CryLaS) at an excitation wavelength of λ=355 nm, with pulse width of about 1 ns and a repetition rate of 100 Hz. The irradiation area of the excitation light was 2.5 mm × 10 mm. A cylindrical lens and neutral density filters were used to adjust the excitation intensities. The emission lights were collected into an optical fiber connected to a spectrometer.

Then, the NPB: 2wt% DCJTB thin film as CC-HTL of OLEDs pumped by EL of the green emission layer (EML) was discussed. AuNPs-layer and the optimized interlayer NPB were deposited into the OLEDs as well to improve the device characteristics. Devices A and B, 4 nm NPB and 6 nm NPB are both used as interlayer for different purposes. ITO, 9,10-di(2-naphthyl)anthracene (AND) doped by 5wt% N,N’-(4,4’-(1E,1’E)-2,2’-(1,4-phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))-bis(2-ethyl-6-methyl-N-phenylalaniline) (BUBD-1), tris(8-hydroxyquinoline)aluminum (Alq3), 8-hydroxyquinoline lithium (Liq) and Al acted as anode, EML, electron transport layer (ETL), electron injection layer (EIL), and cathode, respectively. Devices C and D were fabricated to analyze the influence of AuNPs on hole injection characteristic of the combinational OLEDs, where bathocuproine (BCP) was used as hole blocking layer (HBL). All the organic materials were purchased from Luminescence Technology Corp. (Taiwan) and ITO glass substrate were purchased from CSG Holding Co. Ltd. (China).

All the devices were fabricated by conventional vacuum deposition under a base pressure lower than 2.0×10^4 mbar. The typical deposition rates of organic materials, AuNPs, and Al were 0.6~1.2, 0.1, and 5.0 Å/s, respectively. The active area of the devices defined by the overlap between the electrodes was 4 mm² in all cases.

The electroluminescence (EL) spectra were measured by combining a Keithley 2400 source-meter (Tektronix/Keithley Corp., USA) and a PR-650 spectrophotometer (Photo Research Corp., USA). In addition, extinction and absorption spectra were recorded using a UV-vis spectrophotometer model No. U-3900H (Hitachi Corp. Japan).

3. Results and Discussion

AuNPs-layers with thickness varying from 0.4 nm to 1.6 nm were deposited on glasses, which are multiples of the lattice constant of Au (4.08 Å). The size and density of the AuNPs became larger with increasing thickness of deposited layer. As shown in Figure 1, the normalized absorption spectra of AuNPs-0.8, AuNPs-1.2, and AuNPs-1.6 had well-resolved peaks at 543 nm, 571 nm, and 611 nm. The
AuNPs-0.4 only exhibited mostly featureless absorption data with an onset beginning at around 700 nm due to interband absorption and rising to the ultraviolet (UV) [24]. The peak wavelengths red shifted with the increase of AuNPs size.

Figure 1. The normalized absorption spectra of AuNPs-0.4, AuNPs-0.8, AuNPs-1.2, and AuNPs-1.6 (dashed lines); the normalized absorption spectra and PL emission spectra of NPB and DCTJB (solid lines).

Blending small organic dyes into the context of solid-state lasers is a feasible approach to improve the material performance [25]. In these blends, energy transfer by dipole-dipole coupling (Föster resonance energy transfer, FRET [26] occurs, in which the low concentration of acceptor limited the quenching effect [27]. In this work, organic laser dye DCJTB emitting at red band was chosen as acceptor, while the commonly used hole transport material NPB was employed as donor. The NPB: 2wt% DCJTB thin films were deposited to achieve the low ASE threshold for organic solid-state lasers. The absorption spectra and PL emission spectra of NPB and DCJTB are depicted in Figure 1. The absorption peak wavelengths of NPB and DCJTB were 343 and 511 nm, respectively, while the emission peak wavelengths were 439 and 588 nm. The well overlap between the absorption band of DCJTB and the emission band of NPB indicated good FRET effect. Based on this, cells 0-4 with the structures of glass/AuNPs (x nm)/NPB (4 nm)/NPB: 2wt% DCJTB (100 nm) were fabricated, where the NPB: 2wt% DCJTB was the gain medium, the AuNPs were LSPRs, and the 4 nm layer of NPB was an interlayer to avoid the quenching of dye molecules contacting AuNPs.

The cells 0-4 were pumped from the front side of the organic layer obliquely and the emission was received from the back surface of the glass. The schematic diagram of the measurement is showed as inset of Figure 2. The oblique pumping was set to avoid the appearance of peaks at the 1.5-fold and 2-fold lasing excitation wavelengths (355 nm) when pumped perpendicularly, which would make the ASE peaks of DCJTB too weak to clearly reveal, and the angle of incidence was fixed at 45˚. The back surface emissions of cells 0-4 at the same pumping energy 80 μJ/pulse were gathered in Figure 3. All the ASE intensity of structure with AuNPs-layers were enhanced compared to that of cell 0, and the cell 2 (with AuNPs-0.8) got a maximum 2.69 fold enhancement.

As pumping energy was increased until reached the threshold, a red shift of ASE peak was observed and a slight spike appeared at about 630 nm afterwards. The ASE threshold of cell 2 decreased to 22.13 μJ/pulse compared with that of cell 0 without AuNPs (63.54 μJ/pulse). This yielded the highest quality factor \( Q = \frac{\lambda}{\delta \lambda} = 39.34 \) (at 80 μJ/pulse), while Q values of all structures with AuNPs were higher than that of cell 0 (Q=15.66). Therefore, by concentrating the incident light into local electromagnetic “hot spots”, nanostructured surfaces can lead to increased absorption of the incident light by the gain medium. In addition, MNPs can alter the radiative and the non-radiative decay rates of nearby organic molecules,
changing both the fluorescence lifetime and quantum yield [28]. It means that MNPs can act either as a radiative quencher or radiative enhancer [29-32], depending on the particle size, shape, composition and the distance between the fluorophores and metal nanostructures.

To realize diode pumped organic laser, NPB: 2wt% DCJTB was deposited into OLEDs as CC-HTL. The OLEDs utilizing EL emission of EML to pump the gain medium was an internal color conversion structure sketched as the inset of Figure 3(a), which had a radiative energy transfer mechanism inside. Since the proper organic light-emitting materials, whose emission wavelength were near the 355 nm, were too rare to found, the green light-emitting material BUBD-1 was selected as the EML material. Figure 3 (a) shows that the absorption spectrum of DCJTB perfectly overlapped the emission spectrum of BUBD-1, revealing that the green emission of BUBD-1 could pump the red doping material DCJTB directly and convert the radiative energy to DCJTB sufficiently. The relative energy levels of materials employed in the OLEDs are also included in Figure 3. The low energy barrier between LUMO level of NPB (2.4 eV) and that of ADN (2.6 eV) indicated that a part of carrier recombination might occur beyond the EML. To avoid the recombinational carrier at the interface of NPB and ADN: 5wt% BUBD-1 diffusing into NPB: 2% DCJTB, and to make sure that the red emission of NPB: 2% DCJTB was PL mode rather than EL mode, an interlayer-NPB was inserted between the red emitter (CC-HIL) and green emitter (EML). As NPB exciton diffusion length is 4.9 nm, thickness of the interlayer was set to 6 nm.

Figure 3 (b) depicts the normalized EL spectra of the integrated OLEDs without and with AuNPs (AuNPs-0.8) (Device A and Device B) under different current density. The EL spectra had two peaks respectively at green wavelength region and red wavelength region, which matched the emission peak wavelengths of BUBD-1 and DCJTB. The solid lines are EL spectra of devices A-B under low current density (36 mA/cm²), while device B had an obvious enhancement of red PL. The corresponding CIE coordinates were (0.3672, 0.3529) and (0.4045, 0.3666), declaring the red PL enhancement of Device B as well. The dashed lines are EL spectra under high current density (150 mA/cm²). For device A (OLEDs without AuNPs), the red and green emission ratio of EL spectra remained almost unchanged under different voltages, and it can also be proved from the CIE coordinates. The same phenomenon was also observed in the AuNPs-OLEDs, demonstrating that the AuNPs had not changed the balance between hole mobility of NPB and electron mobility of ADN.

**Figure 2.** ASE spectra of Structure 0-4 at 80 μJ/pulse. The insets are the schematic diagram of the ASE measurement (right) and Q-factors (left).
Figure 3. (a) The normalized absorption spectrum of DCJTB and the emission spectrum of BUBDJ-1, the structure diagram of the integrated OLEDs with AuNPs, and the energy levels of the materials employed in the OLEDs; (b) The normalized EL spectra of Devices A and B under low current density (36 mA/cm$^2$, solid lines) and high current density (150 mA/cm$^2$, dashed lines).

4. Conclusion
AuNPs were introduced to enhance surface ASE of laser dye molecules, the typical donor-acceptor system NPB: 2wt% DCJTB, due to LSPR effect and scattering effect. The NPB: 2wt% DCJTB thin films with AuNPs-layers were optically pumped from an oblique angle and the emission was received from the back surface of the substrate. The gain medium with AuNPs-0.8 achieved the best surface ASE performances, owning 2.69-fold higher peak intensity, lower threshold, and better Q-factor than the neat gain medium. These results reveal that the incorporation of AuNPs would be a simple and feasible way to improve the optically pumped SOLs, which have many advantages in the practical applications, such as easy to combine with optical fibers, convenient to test, densely packed and precisely arranged arrays.

Furthermore, NPB: 2wt% DCJTB was embedded as CC-HTL in an integrated OLED to realize organic solid-state lasers, which could be pumped by EL emission of the EML. The AuNPs deposited on the ITO glass substrate of the OLEDs could also enhance the PL emission of the CC-HTL. The 21.55% ameliorated luminescence, 21.90% higher current efficiency, and 42.11% higher power efficiency at 150 mA/cm$^2$ of AuNPs-OLEDs were also attributed to the improved hole injection caused by AuNPs besides of LSPR and scattering effects. The introduction of AuNPs provides a simple and promising method to realize diode-pumped organic solid-state lasers.

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