Novel Lasing Action in Dye-Doped Polymer Films Coated on Large Pseudotabular Ag Islands

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An ∼15 μm thick polymer film doped (∼5 mM) with a laser dye, when coated on large pseudotabular Ag islands and pumped by a nanosecond laser, generated a single sharp stimulated emission with a bandwidth down to 2.5 nm. We attribute this novel, low-threshold (∼1 mJ/cm^2) lasing action to the surface-enhanced fluorescence of the dyes very near the Ag islands. This highly surface-sensitive lasing concept was supported by the fact that the lasing action was almost completely eliminated by separating the Ag islands and the dye-doped polymer film with a molecularly thin (∼14 Å) spacer.

Since Lawandy et al. reported a remarkable observation of an amplified stimulated emission in a scattering gain medium,[1] there has been growing interest in random lasers (RLs). RLs are now divided into two classes,[2] which are coherent RL that produces a sequence of narrow lines with subnanometer bandwidths and noncoherent RL that gives rise to a single emission peak with a bandwidth typically ∼4 nm at best. In both cases, scattering of photons in the gain medium plays the essential role to increase the light path length,[2,3] thereby providing either a coherent or noncoherent optical feedback mechanism depending on the photon transport mean free path. Here, we address another novel lasing concept that easily yields a single narrow stimulated emission from dye-doped polymer films with a bandwidth smaller than 3 nm when pumped by a nanosecond laser.

As shown in Figure 1, the system simply comprises a dye (rhodamine B)-doped polymer (poly(vinyl alcohol)) film directly coated on a "thick" Ag-island film (TAIF in short). The word "thick" (for island films) is used to emphasize the unique film morphology, consisting of unusually large pseudotabular Ag islands, ∼200 nm in lateral dimensions and ∼50 nm thick (see the inset atomic force microscopy (AFM) image in Figure 1). Unlike the common Ag-island films, TAIF is a highly reflective (0.4−0.6 in specular reflectance in the visible region) film that shows no distinct plasmon-like absorption in the visible region.[4] We have recently shown that TAIF, as such, exhibits a unique, highly efficient fluorescence enhancing capability for nearby dye molecules in the very short range.[4] The enhancement was maximized for dyes located only ∼10 Å away from the TAIF surface, and substantial enhancement occurred even for dyes directly adsorbed on the metal surface. The enhanced fluorescence there could be understood well in terms of a highly radiative mode of oscillating free electron motion in the large Ag islands that constitute TAIF, as induced by the nearby dye emission dipoles. The underlying physics has been established
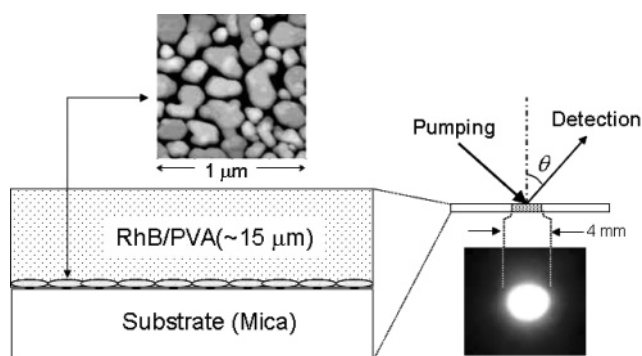
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Figure 1. Structure of the lasing system comprising a dye-doped polymer film coated on large pseudotabular Ag islands as shown by a top-view AFM image on the upper left. The configuration for pumping and detection of the emission is shown on the right along with a photo of a clear lasing spot.

well in the early 1980s by Nitzan et al.[5,6] Importantly, in the sample structure of Figure 1, it is a quite minor fraction among the whole dyes in the system, that is, only those that are located very near the TAIF surface, that can be subjected to the direct fluorescence enhancement by TAIF. Nevertheless, this short-ranged fluorescence enhancement is what most likely causes an intense stimulated emission from the dye-doped polymer film.

TAIF was prepared on a freshly cleaved surface of natural mica according to the DC sputtering method described elsewhere.[4] The dye-doped polymer film was prepared from an aqueous, 4 wt % poly(vinyl alcohol) (PVA) solution in which rhodamine B (RhB; chloride salt) was dissolved typically at the concentration 0.15 mM. A 0.1 mL portion of this solution was spread on TAIF, approximately 10 × 20 mm^2 in area, and dried overnight in the laboratory atmosphere. A much faster drying on a hot plate at 60−70 °C also produced identical results, however. The dried film thickness was not necessarily uniform over the whole area of the sample, ranging from 10 to 20 μm. The net concentration of RhB for the average ∼15 μm film thickness corresponds to typically ∼5 mM. The pump laser
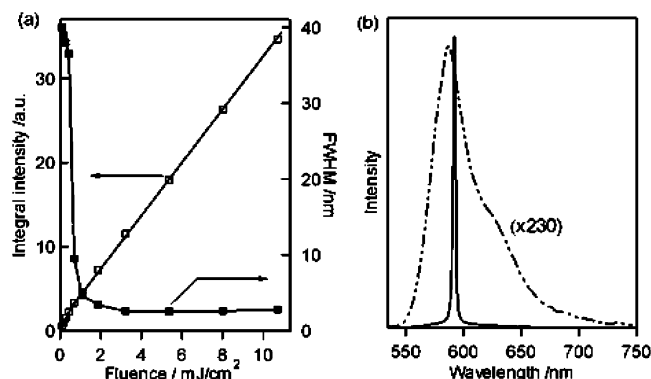
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Figure 2. (a) Wavelength-integrated emission intensity (left axis) and bandwidth (right axis) as functions of pump laser fluence. (b) Examples of emission spectra obtained for two different levels of pump energy below (0.16 mJ/cm²; dashed line) and above (5.4 mJ/cm²; solid line) the lasing threshold.

Figure 3. Measured angular distribution of the intensity of broadband fluorescence emission (*a*) and that of stimulated emission (*b*). The intensity is normalized to that at $\theta = 0°$.

was a frequency-doubled (532 nm), Q-switched Nd:YAG laser (Continuum Minilite II) that produced linearly polarized ~5 ns pulses at a repetition rate of 10 Hz. The emission was collected by a lens typically in the direction of the sample normal ($\theta = 0°$) and spectrally analyzed by a multichannel spectrometer (PMA 11, Hammamatsu Photonics). The limited spectral resolution (~2 nm) of the spectrometer could be improved to ~0.6 nm by deconvolution of the corresponding system response function.

Figure 2a shows how the wavelength-integrated emission intensity and the bandwidth (full width at half-maximum (fwhm)) changed as functions of the pump laser fluence. A sharp transition from normal to stimulated emission is clearly evidenced by the rapid decrease of bandwidth from ~37 to ~4 nm over the considerably narrow range of fluence between ~0.4 and ~1 mJ/cm². Above this lasing threshold (i.e., ~1 mJ/cm²), the emission became still narrower down to 2.5 nm in the region 3−8 mJ/cm². Examples of the emission spectra obtained at two different levels of pumping, one below the lasing threshold and the other in the region producing the smallest bandwidth of 2.5 nm, are shown in Figure 2b. Further increase in the pump laser fluence had a tendency to slowly increase the bandwidth again (to 3−4 nm). Moreover, above ~13 mJ/cm² (beyond the range plotted in Figure 2a), TAIF underneath the polymer film began to be irreversibly damaged by the pump laser. Although the lasing action still persisted under such high fluence conditions, the corresponding bandwidth exceeded 5 nm, and once TAIF was damaged in this way, the narrowest emission, 2.5 nm in fwhm, could no longer be restored under any pumping conditions. It should also be noted that in Figure 2a the sharp transition from the normal to the stimulated emission is reflected also in the integrated emission intensity profile. Namely, although it appears that the integrated intensity steadily increased with fluence without any saturation behavior, actually a noticeable change in slope occurred (to make a kink) at approximately the same low fluence (~0.4 mJ/cm²) as that where the bandwidth began to drop sharply.

The strong stimulated emission had some other unique characters. First, it was considerably more polarized in the same direction as the polarization of the pump laser ($I_\parallel/I_\perp$ ratio of ~1.6) than the normal broadband emission ($I_\parallel/I_\perp$ ratio of ~1.2 or less). Second, the photo of a clear lasing spot included in Figure 1 shows no significant blurring outside the pumped area. This feature makes the observed stimulated emission be clearly distinguishable from the phenomenon known as amplified spontaneous emission (ASE),[7] since in the present system ASE
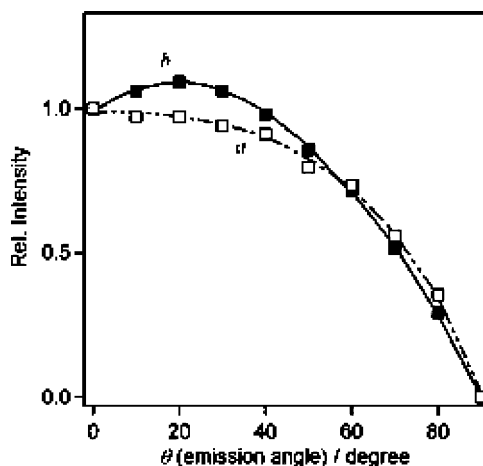
(if any) should have developed parallel to the film plane. Though ASE can also produce a significantly narrow emission band, it is far less laserlike than and thus incomparable with the TAIF-induced lasing action. The directional character of the present stimulated emission can be examined more quantitatively in terms of its angular distribution; see Figure 3. In the case of normal broadband emission, its angular dependence followed in good approximation the standard law for dyes homogeneously distributed in a medium with refractive index *n*, that is, cos $\theta/(n\sqrt{n^2-\sin^2\theta})$.[8] In contrast, the angular dependence of the stimulated emission was broadly peaked at $\theta \sim 20°$.

For understanding the mechanism of the TAIF-induced novel lasing action, it should be stressed again that the dyes subjected to the short-ranged fluorescence enhancement by TAIF are strictly limited to those that are well within ~100 Å away from the TAIF surface. If the distribution of RhB's in the ~15 μm thick PVA film were totally homogeneous, then the effective dye fraction for that direct fluorescence enhancement would be less than 0.1%. In practice, however, RhB chlorides can make specific adsorption on TAIF, as assisted by the strong interaction between the Ag surface and the chloride counterions.[9] This in turn leads to a roughly monolayer (of the order of 10^{13} molecules/cm²) adsorption of RhB, which is equivalent to ~1% or more of the whole dyes in the system. What is responsible for the present lasing action is most probably the TAIF-enhanced fluorescence for these dyes that are concentrated at the TAIF/polymer interface.

To verify the above interpretation, we fixed on TAIF a molecularly thin spacer, an ~14 Å thick self-assembled monolayer of 11-mercaptoundecanoic acid, before coating the dye-doped polymer film. This satisfactorily prevents the specific RhB adsorption onto the TAIF surface. Figure 4a shows that even this trivial surface modification almost completely eliminated the sharp stimulated emission, though some peak narrowing was still noticeable. As a result, the wavelength-integrated emission intensity as a function of pump laser fluence (Figure 4b) now manifested a clear saturation behavior. A similar strong suppression of the lasing action was observed also with a more inert spacer, as prepared by spin coating a highly diluted spin-on glass solution (Honeywell International Inc.). Thus, the binding of the sulfur atoms to the Ag surface in the case of the thiol spacer should have no relevance for the result. Such a dramatic effect of a molecularly thin spacer supports the fact that the lasing action in the present system is
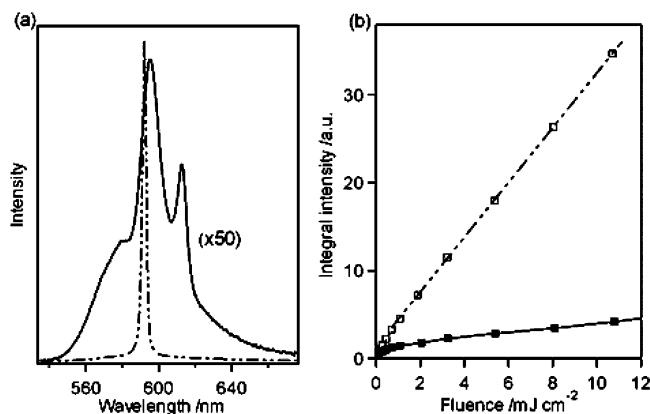
Figure 4. (a) Typical emission spectra and (b) wavelength-integrated emission intensity profiles as functions of pump laser fluence, showing the dramatic effect of a molecularly thin spacer between TAIF and the dye-doped polymer film, eliminating the lasing action. The solid-line data are for samples with the spacer, and the dashed-line data are a reproduction (for reference) of those presented in Figure 2.

indeed a substrate-surface-induced phenomenon without any special optical feedback mechanism.

Since the fluorescence lifetime of RhB's in the relatively rigid PVA matrix is expected to be comparable to their normal radiative decay time, 3−4 ns,[10] and thus to the ∼5 ns pump pulse duration, the number of excitation−emission cycles allowed for each dye molecule in the absence of amplified emission is naturally limited. This is the obvious reason for the intensity saturation in Figure 4b, beginning at around 1 mJ/cm². This in turn means that, at the lasing threshold in Figure 2, which was also around 1 mJ/cm², a sufficiently large number of excited-state RhB's for potential lasing is generated in the dye-doped polymer film. Unfortunately, we are not yet sure of the exact radiative decay time for the TAIF-enhanced fluorescence. However, earlier studies[11,12] have shown that the fluorescence lifetimes of molecules near Ag islands were shortened by as much as 3 orders of magnitude without being substantially quenched. This in turn proves a dramatic decrease in the radiative lifetime. For the highly efficient TAIF-enhanced fluorescence, we then expect that the net radiative lifetime could be by at least 1 or 2 orders of magnitude shorter than that for the normal fluorescence emission. In the case of RhB's directly adsorbed on TAIF, which we proposed to play the dominant role for the lasing action, it may possibly reach some picosecond time regime. This much faster emission can then cause an avalanche of stimulated emission completed in a similar time scale to this TAIF-enhanced fluorescence for all of the other excited-state RhB's in the polymer bulk. The overall emission

is thus strongly narrowed at the wavelength of maximum gain. Also, the cycle of excitation and amplified emission can be repeated many times in the ∼5 ns pump pulse duration, so that the integrated emission intensity no longer saturates as a function of pump laser fluence. According to this lasing scheme, the polarization and the angular distribution of the amplified emission should basically follow those of the TAIF-enhanced fluorescence as the trigger light. The stronger polarization of the stimulated emission than that of the normal fluorescence signal is thus of no surprise. As for the angular distribution, however, we should also take into account the fact that the gain length for the stimulated emission becomes larger at larger off-normal angles. This additional angular factor explains why the amplified emission was maximized not at $\theta \sim 0°$ but at $\theta \sim 20°$ (Figure 3).

Finally, the effects of dye concentration in the PVA film, not detailed here, were also consistent with the proposed lasing scheme. The lower the concentration, the smaller the gain of the medium. We could no longer observe the lasing action at dye concentrations lower than ∼1 mM. In the opposite regime, the pump laser is so effectively absorbed by the dyes in the polymer bulk that it becomes harder to reach the dyes very near (adsorbed on) the TAIF surface that provide the trigger light for lasing. This inevitably increases the lasing threshold and leads to a lesser degree of narrowing of the lasing peak. At a dye concentration of ∼15 mM, for example, the lasing threshold increased to ∼5 mJ/cm² and the smallest bandwidth achieved so far was ∼4.5 nm.

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