A Random Laser Production Using Fluorescein Dye Doped TiO$_2$ Nanoparticles

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Abstract
A random laser has been produced using Fluorescein dye solution in water, with concentration of (8×10$^{-5}$ M); doped with (0.001 g) TiO$_2$ Nanoparticles with the particle size of (15.7 nm). A blue diode laser of 450 nm wavelength has been used as an optical pumping source. The wavelength of the random laser was 523 nm and the intensity was 5.44 mW.

Keywords: random laser, Fluorescein dye, TiO$_2$ Nanoparticles, surface plasmon resonance, fluorescence enhancement.

Introduction
Random lasers are unusual light sources that emit coherent light without any reflecting mirrors (cavities) that are part of a traditional laser [1, 2]. As an alternative, the light inside a random laser is confined by multiple scattering in a disordered medium and can be well amplified. The weakness is that random lasers emit their light at many altered frequencies and in all directions [3, 4, and 5]. Scientists have then thought about how to ‘domesticate’ random lasers by making both their directionality and emission spectrum externally tunable [6, 7, and 8]. A tunable random laser embraces huge promise for a range of applications. It could be used as a multiuse device with a modified functionality that is determined not by its design but somewhat by external control knobs.

Since the report of laser action from an optically pumped solution containing high-gain laser dyes with TiO$_2$ nanoparticle as a scattering material [9], there has been rising interest in accepting the basic mechanisms responsible for the detected excitation threshold behavior, the linear input–output features, and the narrow emission line width [10, 11].

Interference can happen through multiple scattering, which leads to a granular distribution of the intensity termed speckle. In certain random materials, interference can cause an effect named light localization [2], which is the optical equivalent of Anderson localization of electrons [2, 10].

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Localization can only have effect in optical materials that are very strongly scattering, the condition being that the mean free path \( l \) becomes smaller than the reciprocal wavevector \( (kl \leq 1) \).

Lasing action of xanthene dyes cover a wavelength section from 500 to 700 nm and are usually very active. Most of the commercial dye lasers are from this class, Fluorescein (F) is one of broadly used laser dyes [12]. Fluorescein dye appears in various forms, at different pH values, these forms are cation, neutral molecule, monoanion and dianion, causing its absorption and fluorescence spectra highly dependent on pH. At pH values beyond 6.4, the dianion is the most common [13] (as in this work, where the pH of distilled water is 7).

In this research, Fluorescein dye mixed with TiO$_2$ Nanoparticle has been used to produce a random laser.

**Materials and methods**

In this experiments, the gain medium consisted of a Suspension of 0.001g of TiO$_2$ anatase nanoparticles (with an average size of 15.7 nm, Purity: 99%, Nanoshel LLC) in Fluorescein (C$_{20}$H$_{12}$O$_5$, BDH, $M_w$ = 332.306 g/mol) with 10 ml of distilled water, used in this experiments. The solution of dye samples of concentrations (1x10$^{-5}$ M, 2x10$^{-5}$ M, 4x10$^{-5}$ M, 6x10$^{-5}$ M and 8x10$^{-5}$ M) were prepared using the following equation [14]:

\[
m = C \frac{V}{M_w}
\]

where \( m \) is the weight of the dye needed to obtain the desired concentration, \( C \) is the required concentration of the dye, \( V \) is the volume of solvent for the dye, and \( M_w \) is the molecular weight of the dye. The dye samples of all used concentrations are shown in Figure-1.

![Figure 1- Prepared samples of Fluorescein dye of all used concentrations (1, 2, 4, 6 and 8) x10$^{-5}$ M.](image)

All samples were prepared using hot plate stirrer till the TiO$_2$ nanoparticles homogeneously diffused through the Fluorescein solution at room temperature (30°C). Fluorescence spectra were measured using spectrofluorophotometer (SHIMATDZU RF-5301pc).

Figure-2, shows XRD pattern of TiO$_2$ nanoparticles, measured using SHIMADZU XRD – 6000, Cu K\(\alpha\). The XRD spectrum shows that the TiO$_2$ nanoparticles are crystalline, tetragonal crystal system with lattice constant of \( (a = 3.7850 \text{ Å}, c = 9.5140 \text{ Å}) \). Strong diffraction peaks at 25º (101), 48º (200) and 37º (004) indicating TiO$_2$ in the anatase phase.
Continuous wave laser diode (T4085-L) of 1 W output power and 450 nm wavelength, has been used for the optical pumping. A laser power meter (SANWA-LP1) with (Silicon photodiode, 400～1100 nm range) used at 90° with the cell, which contains the solution of the sample, to measure the produced random laser intensity.

**Results and Discussion**

Figure-3, shows the fluorescence spectra for the concentrations of (1x10⁻⁵ M, 2x10⁻⁵ M, 4x10⁻⁵ M, 6x10⁻⁵ M and 8x10⁻⁵ M) without TiO₂ nanoparticles, and Figure-4, Shows the fluorescence spectra for the same concentrations with (0.001g) TiO₂ nanoparticles. Table-1, present the details of these results.
Adding 0.001g of TiO$_2$ nanoparticles to the dye, quenched the fluorescence spectra of this dye, except for (6x10$^{-5}$ M and 8x10$^{-5}$ M) concentrations where the fluorescence has been enhanced. Some cases had made a very small redshift of about 1 nm.

When the concentration of fluorescent dyes is high, inner filter effects and aggregation can lower the fluorescence intensity. In particular, the photons emitted at wavelengths corresponding to the intersection between the absorption and emission spectra may be reabsorbed (auto-absorption by solution), as can be seen from the Figure-3.

Table 1-Fluorescence results of a number of dye concentrations with, and without TiO$_2$ nanoparticles.

<table>
<thead>
<tr>
<th>F (M)</th>
<th>$\lambda_f$ (nm)</th>
<th>intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1*10^{-5}$</td>
<td>514</td>
<td>47.48</td>
</tr>
<tr>
<td>$1*10^{-5}$</td>
<td>514</td>
<td>180.82</td>
</tr>
<tr>
<td>$2*10^{-5}$</td>
<td>517</td>
<td>119.62</td>
</tr>
<tr>
<td>$2*10^{-5}$</td>
<td>516</td>
<td>281.94</td>
</tr>
<tr>
<td>$4*10^{-5}$</td>
<td>520</td>
<td>164.05</td>
</tr>
<tr>
<td>$4*10^{-5}$</td>
<td>520</td>
<td>169.95</td>
</tr>
<tr>
<td>$6*10^{-5}$</td>
<td>522</td>
<td>166.32</td>
</tr>
<tr>
<td>$6*10^{-5}$</td>
<td>521</td>
<td>96.22</td>
</tr>
<tr>
<td>$8*10^{-5}$</td>
<td>523</td>
<td>143.66</td>
</tr>
<tr>
<td>$8*10^{-5}$</td>
<td>522</td>
<td>61.36</td>
</tr>
</tbody>
</table>

From Figure-3 and Table-1, it is clear that the fluorescein dye with TiO$_2$ nanoparticles has a tangible enhancement in the fluorescence, within the concentrations of (6x10$^{-5}$ M and 8x10$^{-5}$ M), this can be explained by local field enhancement of the surface plasmon. Proving that adding TiO$_2$ nanoparticles can eliminate the inner filter effects and aggregations (which lowers the fluorescence intensity at high concentrations).

The sample of (8x10$^{-5}$ M) concentration of the Fluorescein dye with 0.001g of TiO$_2$ nanoparticles, was selected to produce a random laser, because it showed the maximum enhancement of the fluorescence.

The setting of the random laser production is shown in Figure-5.
Figure 5-A diagram of the experiment for producing the random laser, (a) setting of the experiment and measuring the intensity, (b) experiment before using the pumping source, and (c) experiment using the pumping source and producing the random laser.

Figure 6, shows the wavelength of the random laser, the maximum intensity is at 523 nm wavelength ($\lambda_f$). The intensity of this laser was 5.44 mW.

Figure 6-Wavelength and Fluorescence intensity of the random laser.
For rising the performance of random lasers, it is vital to enlarge the gain volume and the scattering strength of the random nanostructures. Whereas it is hard for some materials to achieve a large gain volume and a strong scattering strength at the same time, other nanoparticles like TiO$_2$ have such ability. First, these nanoparticles have a large scattering cross section in the same volume. Second, the TiO$_2$ nanoparticles have surface plasmon resonance (SPR) which can confine the light near the surface to allow high gain for lasing. That means the TiO$_2$ nanoparticles can scatter light with high efficiency and enhance light locally over surface plasmon resonance [15].

**Conclusion**

In conclusion, we have clearly demonstrated that random laser of 5.44 mW intensity, can be produced from mixing Fluorescein dye of concentration (8×10$^{-5}$ M) with (0.001g) of TiO$_2$ nanoparticles in distilled water. This concentration and amount of TiO$_2$ nanoparticles were not used before to produce random laser in distilled water. This method of producing such laser, is easy and relatively cheap.

References