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Emission enhancing characteristics in electrochemiluminescence devices by 9,10-diphenylanthracene dye-highly scattering TiO_2 solid-nanoparticle mixture

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Abstract Emission enhancing effects in electrochemiluminescence (ECL) device of 9,10-diphenylanthracene (DPA) dye-solution containing a mixture of highly scattering TiO_2 nanoparticles were observed. We confirmed experimentally that there exists an optimum quantity of the highly scattering TiO_2 nanoparticles assisting the emission enhancement in the ECL device of DPA solution. An agreement, between experiment and theory, of the optimum quantity depending on particle size of nanoparticles is discussed and confirmed.

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1 Introduction

Traditional organic light-emitting devices (OLEDs), consisting of solid-state thin films with a typical thickness of about 100 nm [1, 2], have attracted a great deal of attention, and small-size flat-panel displays using OLEDs have recently been commercialized. It was also demonstrated that the application of organic dye solutions are used as the active medium for light emission [3], in which it was proved that electrogenerated chemiluminescence [or electrochemiluminescence (ECL)] was responsible for the generation of the light. Electrically pumped laser action was also observed [4] from a circulation cell employing an organic dye solution with a resonant cavity. On the other hand, the results of experiments on laser action of optically pumped rhodamine (RH) dye solutions in highly scattering media consisting of TiO_2 nanoparticles interested many workers in the laser field [5, 6]. It was reported that multiple light scattering in an appreciably scattering and diffusive medium can trap both excited and emitted photons in a small spatial region so that the gain exceeds the loss [5, 6].

Some interesting papers have reported on lasing emissions from dye-doped microdroplets [7] at discrete wavelengths corresponding to morphology-dependent resonances (MDRs) of the sphere. We have first reported the RH6G microdroplet dye-laser action exhibiting well-defined thresholds along with appreciably increased emission intensities containing highly scattering poly(methyl methacrylate) solid nanoparticles [8]. Furthermore, Intralipid solution (soft nanoparticles) as highly scattering turbid medium to obtain laser action in RH6G dye [9, 10] and in biological tissues [11, 12] has been successfully used. The first laser action as further novel approaches using active particles of red fluorescent-powder [13] and new biochemical species of riboflavin (vitamin B_2) [14] contained in liquid microdroplets by mixing Intralipid solution was also reported.

We were trying to confirm whether the multiple light scattering feature, mentioned above, is significantly effective also in the emission of the ECL devices. There are some advantages associated with ECLs. The most significant advantages are the simplicity of the process of device fabrication, its large-area processing capability, and its essential pinhole-free feature because of using solution as an active material.

2 Experimental and results

In this work, we describe the fabrication of the ECLs with a simple method and experimental results of emission

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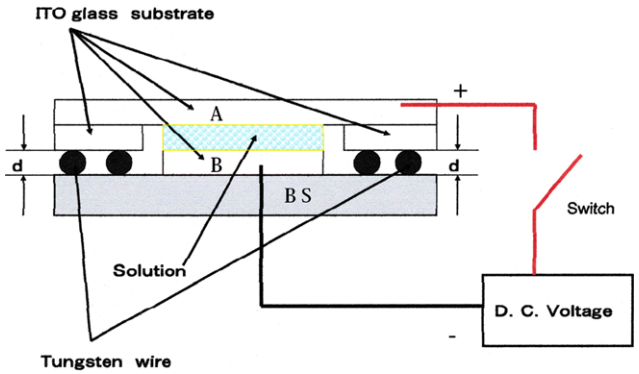

Fig. 1 Construction of ECL cell. A: upper ITO electrode; B: lower ITO electrode; BS: back-glass substrate; +, −: positive and negative bias of DC voltage supply, respectively

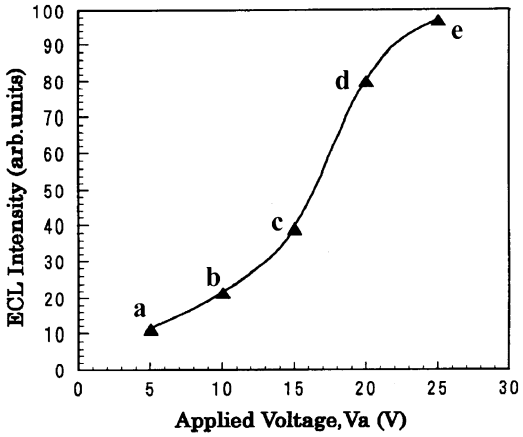

Fig. 2 Emission peak-intensity from neat (without scatterers) DPA ECL depending on applied voltage V_a. $C = 5 \times 10^{-3}$ mol/l, $d = 2.5$ μm, $V_a = 5$ (a), 10 (b), 15 (c), 20 (d), and 25 V (e)

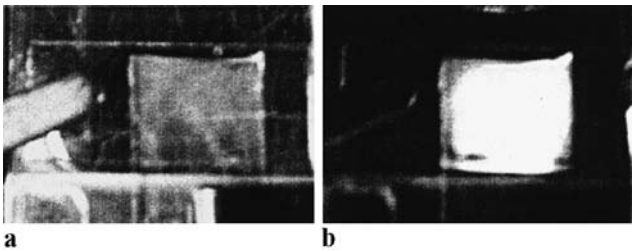

Fig. 3 Actual view of the pre-biased ECL cell ($V_a = 0$ V) in (**a**) and light-emitted ECL in (**b**). $C = 5 \times 10^{-3}$ mol/l, $d = 2.5$ μm, and $V_a = 20$ V

characteristics of the ECLs. We have selected as the active material of the ECLs 9,10-diphenylanthracene (DPA; $(C_6H_5))_2C_{14}H_8$, purchased from Nacalai Tesque Inc.) dye of the scintillation grade, based upon the experimental results whereby the lasing action was observed by DC voltage driver [4], and by UV N_2-laser pumping about 40 years ago (Ref. [10] in [4]), as the result of the DPA active material with high quantum efficiency. It should be remarked that the emission enhancement only appears from the ECL device of DPA solution by mixing suitably with highly scattering TiO_2 solid-nanoparticles (presented by Ishihara Industry Co. Ltd.). Our ECL cell consists of a DPA solution layer sandwiched between two transparent indium-tin-oxide (ITO)/glass substrates. The fabrication process of the ECL cell is fairly simple as shown in Fig. 1. First, several drops of DPA solution (DPA-DMF) in N, N-dimethylformamide (DMF) are deposited on top of the lower ITO/glass substrate (B in Fig. 1) on the back-glass substrate (BS). Next, another (the upper, A in Fig. 1) ITO/glass substrate, through one more ITO/glass substrate with the same thickness, is placed on top of the first ITO/glass substrate with the two ITO electrodes facing each other and the DPA-DMF solution situated in between the two ITO/glass substrates. Then, these two ITO/glass substrates are pushed against each other by the application of an external force, resulting in a given electrode spacing (d in Fig. 1), which depends on a diameter of tungsten-wire as a spacer. Thus, the dye solution layer is controlled by a diameter d of tungsten wires, $d = 2.5$, 5, and 10 μm, which are comparable with that in the previous report [4]. The upper ITO electrode (A in Fig. 1) is positively biased against the lower ITO electrode (B in Fig. 1), and the emitted light from the ECL cell is detected from the upper ITO electrode.

We have examined DPA-DMF dye solution prepared in rather higher DPA concentration C, through the preliminary experimental results, using DMF as the solvent. Emission characteristics of the fabricated ECLs were measured using an optical multichannel analyzer (OMA; Ocean Optics, USB4000), by applying DC voltage up to 25 V. The emission peak-intensity from the neat (without scatterers) DPA-DMF ECL is plotted in Fig. 2, depending on the applied voltage V_a, under the conditions of $C = 5 \times 10^{-3}$ mol/l and $d = 2.5$ μm. It is found in Fig. 2 that the voltage for the onset of photon emission is about 5 V, and a tendency of saturation of the ECL intensity appears above $V_a = 20$ V. It was observed that the emission spectra, over the range from 400 nm to 500 nm, are almost analogous to the free-space spectrum in the previous report [4].

The actual view of the pre-biased ECL cell (at $V_a = 0$ V) is displayed in (a) in Fig. 3. The crossed area of the upper and the lower ITO/glass electrodes is approximately 10×10 mm^2. It seems in (b) in Fig. 3 (the case of the neat solution), under the conditions of $C = 5 \times 10^{-3}$ mol/l, $d = 2.5$ μm, and $V_a = 20$ V, that the rather homogeneous emission occurs over the crossed area of the electrodes.

It is exhibited in Fig. 4 that the emission peak-intensity, from the neat DPA-DMF ECL under the conditions of $C = 5 \times 10^{-3}$ mol/l and $V_a = 20$ V, increases as the electrode spacing d decreases.

Experiments were performed on the spectral and intensity properties of emitted light, in comparison with the neat (without scatterers) and the mixture with scatterers (TiO_2

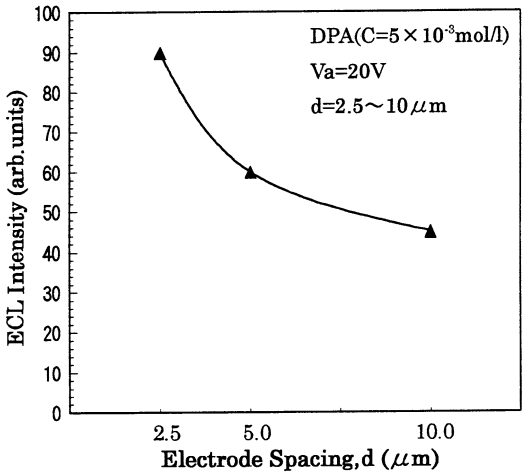

Fig. 4 Emission peak-intensity against electrode spacing d, from neat (without scatterers) DPA-DMF ECL. $C = 5 \times 10^{-3}$ mol/l and $V_a = 20$ V

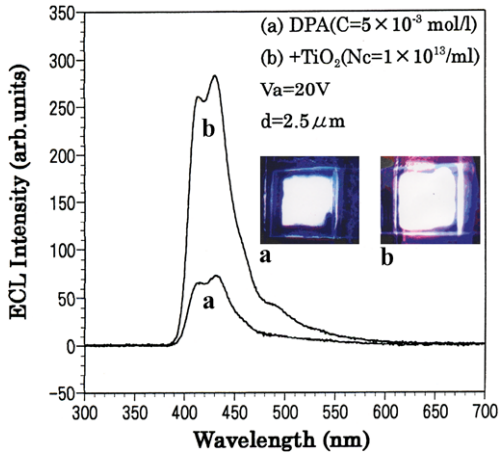

Fig. 5 Comparison of ECL emission peak-intensity. (a) neat and (b) with scatterers. $N_c = 10^{13}$/ml, DPA-DMF ECLs. $C = 5 \times 10^{-3}$ mol/l, $V_a = 20$ V, and $d = 2.5$ μm. *Inset*: Visual view of the DPA-DMF ECLs in (a; *left*) neat and in (b; *right*) with TiO_2 scatterers ($N_c = 10^{13}$/ml)

solid nanoparticles with an average diameter φ of 150 nm). The comparison of the ECL emission spectrum is demonstrated in Fig. 5, without (a; neat) and with TiO_2 scatterers (b; the case of nanoparticle contents N_c of 10^{13}/ml), under the conditions of $C = 5 \times 10^{-3}$ mol/l, $V_a = 20$ V, and $d = 2.5$ μm. It is recognized that the spectral position of the emitted light is almost identical in the wavelength region in the both cases of without (neat; a in Fig. 5) and with scatterers (b in Fig. 5). It is noted that the ∼3.5 times enhancement of the peak ECL-intensity is obtained by mixing suitably with highly scattering TiO_2 nanoparticles, compared with the neat solution.

The visual view of the DPA-DMF ECLs is displayed in (a; left) neat, and in (b; right) with TiO_2 scatterers ($N_c = 10^{13}$/ml), in the inset in Fig. 5, in which the conditions of the

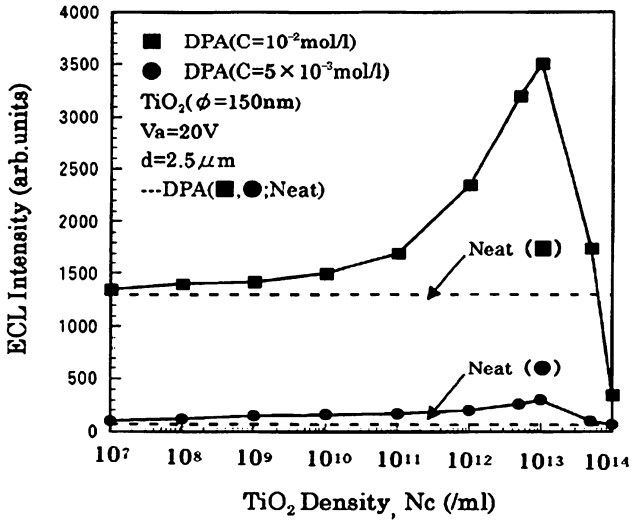

Fig. 6 Comparison of ECL emission peak-intensity with scatterers contents N_c. *Solid circles*: $C = 5 \times 10^{-3}$ mol/l; *solid squares*: $C = 10^{-2}$ mol/l; DPA-DMF ECLs. $V_a = 20$ V and $d = 2.5$ μm. *Horizontal dotted lines* correspond to the intensities from the individual neat (without TiO_2 nanoparticles) ECLs for dye concentration

comparison are same as for Fig. 5. It is clearly recognized in the inset in Fig.5 that the much stronger emission occurs in (b) (with the scatterers) compared to in (a) (neat).

Furthermore, the condition of the contents of TiO_2 solid nanoparticles N_c into the DPA-DMF dye solution is carefully examined. The experimental results of emission peak-intensity, depending on the N_c contents, are plotted in Fig. 6, in comparison with the cases of $C = 5 \times 10^{-3}$ mol/l mentioned above along with the much higher DPA concentration of $C = 10^{-2}$ mol/l, under the conditions of $V_a = 20$ V and $d = 2.5$ μm. The additive amounts of $N_c = 10^{13}$/ml into the neat solution in Fig. 5 were nearly optimum from the maximum intensity of the emission of DPA-DMF ECLs. One can see clearly from Fig. 6 that the ECL mixed suitably with TiO_2 solid nanoparticles yields the enhancement of the emission intensity. By adding a scattering medium in the neat solutions, the higher emission gain may build up through multiple light scattering in a small spatial region [5, 6]. It is recognized also in Fig. 6 that twice the DPA concentration produces the emission intensity with one-order magnitude higher.

In order to clarify the contribution to the emission intensity of ECLs of scatterers, further experiment was carried out with different average diameters of scatterers. The results of emission peak-intensity, depending on the N_c contents, are demonstrated in Fig. 7, in comparison with the cases of TiO_2 solid nanoparticles with $\varphi = 150$ nm in solid squares and $\varphi = 250$ nm in solid circles, DPA-DMF ECLs, under the conditions of $C = 10^{-2}$ mol/l, $V_a = 20$ V, and $d = 2.5$ μm.

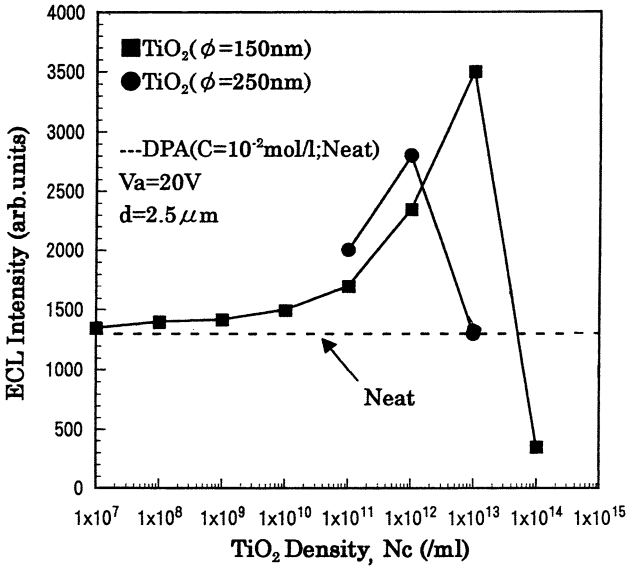

Fig. 7 Comparison of ECL emission peak-intensity with scatterers contents N_c. *Solid squares*: TiO_2 solid nanoparticles with $\varphi = 150$ nm; *solid circles*; $\varphi = 250$ nm; DPA-DMF ECLs. $C = 10^{-2}$ mol/l, $V_a = 20$ V, and $d = 2.5$ μm. *Horizontal dotted line* corresponds to the intensity from the neat (without TiO_2 nanoparticles) ECL

3 Discussion

It is found in Fig. 2 that the voltage for the onset of photon emission is about 5 V (a), and a tendency of saturation of the ECL intensity appears above $V_a = 20$ V (d), and nonuniform arc-discharges often occur when $V_a > 25$ V. In Fig. 2, the increasing of emission intensity ((b)–(d)) is rather superlinear with the increasing of the applied voltage ($V_a = 10$–around 20 V). We think a kind of stimulated-emission effects like amplified spontaneous emission (ASE) might happen around here, along with the increasing of emission intensity. Rather smooth increase of emission light-intensity with increase of V_a might be due to increase of carrier-injection from the both electrodes, resulting in increase of carrier-recombination rates, as the same as the conventional ELs.

According to the prediction by Mie theory, at fixed wavelength λ (400–500 nm in Fig. 5) and index of refraction of material, based on the approximation of small size parameter x ($x = \pi\varphi/\lambda$ is approximately unity, which is valid in the present experiment), we can see that the mean transport length l_t is estimated to be approximately a few μm, in the solutions with the size of scatterers $\varphi = 150$ nm and $N_c = 10^{13}$/ml. This estimated l_t is comparable with the sample size (ECL thickness) in our experiment, and it is considered that the corresponding value $N_c = 10^{13}$/ml is nearly optimum. The drastic change of emission intensity at $N_c > 10^{13}$/ml beyond the optimum value resembles to our previous results [8].

Furthermore, by Mie theory, the efficiency factor of scattering Q_{sca} is proportional to φ^4 at fixed wavelength λ and index of refraction of material, based on the approximation of small size parameter x ($x = \pi\varphi\lambda$) [15]. From this result we can see that the scattering cross-section C_{sca} varies as size of the particle to the sixth power. If the emission is optimum at the same transport length l_t, in the solutions with the different sizes of scatterers $\varphi = 150$ nm and $\varphi = 250$ nm, the ratio of C_{sca} for the ratio of $\varphi = 250$ nm/$\varphi = 150$ nm is approximately 20, the ratio of N_c in the optimum contents for the ratio of $\varphi = 150$ nm/$\varphi = 250$ nm is approximately 20 because the N_c contents is inversely proportional to the cross-section under the present assumptions, in which the approximation of small size parameter mentioned above is valid because $x = \pi\varphi/\lambda \approx 1$.

It is interpreted that the value of scatterers contents to the optimum emission peak-intensity in the experiments is in good agreement with the theoretical expectation, under the present assumptions, however, further investigation is needed for comparison of the previous (optical pumping) and present (electrical pumping) works. Moreover, spectral (blue) shift with scatterers appeared in the previous work [8], but not appeared in the present one, also is needed for further investigation.

4 Conclusions

We have fabricated an ECL device by a simple method and presented the experimental results of interesting emission properties from the ECL devices containing 9,10-diphenylanthracene solution by mixing with/without TiO_2 solid nanoparticles as highly scattering media. Our noteworthy findings would suggest that the present method utilizing highly scattering medium could be widely applied to a large number of dyes and very attractive even for enhancement of ECL emission and for lasing of liquid microdroplets such as in our previous results.

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