Light Capture Enhancement for Thin Films of Photosensitive Materials by Multilayer Design with a Diffuse-Reflecting Metal Interface

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Abstract

This paper presents a simple method or system to enhance (by 10 times or more) the light capture efficiency of ultrathin films (including molecular adsorbates) of photosensitive materials (specifically organic dyes) by placing them on top of a thin dielectric layer (transparent) that covers a diffuse-reflecting metal (Ag) surface. The method utilizes in part a tri-layer anti-reflection design, plus a novel design that not only leads to more effective confinement of the incident photons but also allows the consequent evanescent wave to play significant role in increasing the overall light capture efficiency.

Introduction

The efficiencies of photo-imaging and other opt-electronic devices based on photosensitive materials critically depend on their light absorbing capability. However, the optical thickness of such materials, as used in practical systems, is often so small that the net light capture (absorption) efficiency hardly exceeds ~10%. The spectral sensitivity of the silver halide photographic materials indeed rests upon the limited light absorptivity of J-aggregates of spectral sensitizing dyes that are adsorbed on the silver halide grain surface typically with a sub-monolayer coverage. The J-aggregates, particularly the types of mixed J-aggregates with a unique hetero-excitonic state that facilitates the intra-aggregate charge separation, can also be used to construct a photoelectric device with a markedly high quantum yield.[1,2] However, here again, it is difficult to format the J-aggregate for it to function in a multilayered structure, so that the maximum light absorptivity is likewise limited to ~10 % at maximum.

If the light capture efficiency of these molecularly thin layers could somehow be increased by e.g., 10 times, it then follows that the majority (~100 %) of the incident photons may be captured by the same layer with the original light absorptivity of only ~10 %. The light capture enhancement by an order of magnitude or more thus gives a large technological impact in many related fields. In this paper, the author presents a simple method to make this come true, though unfortunately the method may not necessarily be compatible with the silver halide photographic materials.

It is clear that the lower the absorptivity intrinsic to a thin absorber layer, the greater the impact of the enhanced light absorption. Also, what is essential is not just the light absorptivity itself, but how the consequent photophysical and/or photochemical outputs can be enhanced accordingly. In this report, the author chose a thin (less than 10 nm) dye-doped polymer (PVA) film as a test absorber layer, for which the intrinsic light absorptivity is of the order of ~1% or less. The extent of enhanced light absorption was monitored by the intensity of fluorescence in the same excitation condition, rather than by the change of absorptivity that is not necessarily measured accurately for the proposed system involving a diffuse-reflecting metal surface.

Principle of Enhancement

Of the two factors that contribute to the enhanced light absorption in the proposed system, one is directly correlated with the well-known thin-film anti-reflection structures.[3] The simplest structure has a tri-layer configuration (see Figure 1), comprising a transparent dielectric spacer with a thin (typically ~10 nm thick) absorber layer on one face and a good reflector (such as Ag or Al mirror) on the other face. By adjusting the absorber layer thickness and that of the transparent spacer, the overall reflectance of the tri-layer structure can be made very close to zero; thus an almost perfect anti-reflection condition can be easily obtained. This phenomenon equivalently means that the incident light is almost totally absorbed by the thin absorber layer, which can be understood as originated from the constructive interference between the incident and reflected (by the reflector) light that gives rise to an amplified electric field at the position of the thin absorber layer.

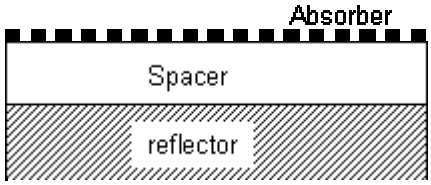

Figure 1 *Standard tri-layer configuration for anti-reflection*

Importantly, there is a spacer thickness around which the above condition for the constructive interference (i.e., enhanced light absorption) is approximately met in the whole range (400–800 nm) covering the visible region. This means that the required condition for the constructive interference is not very strict. In the case of dielectric material with a refractive index of n=1.3, this optimum spacer thickness is at ~100 nm. A typical enhancement factor in this condition can be theoretically predicted according to the Fresnel formalism for an arbitrary absorber layer, if only its complex refractive index is known. Figure 2 shows an example for a hypothetical absorber that mimics the absorption of a thin organic dye layer; where the calculated absorptivity of the model dye layer on glass surface (~10% at the absorption peak) is compared to that of the same dye layer but in the tri-layer configuration with an optically flat Ag mirror as the reflector. It can be seen that the tri-layer structure brings about approximately 5 times absorption enhancement. Note, however, that in order to

achieve the ~100% absorption (or the perfect anti-reflection condition), the absorber layer has to be made much thicker so that the absorber layer alone can have the absorptivity of at least ~30%.

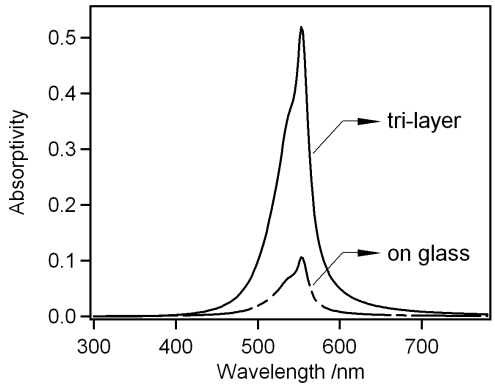

Figure 2 *Calculated absorption spectra of a model dye layer on glass surface and in the tri-layer configuration with Ag mirror as the reflector and with 100 nm spacer (n=1.3).*

A novel trick to achieve a large additional gain in the light absorptivity is to replace the optically flat reflector by a diffuse reflecting mirror with a surface corrugation relatively mild in the Z direction but of sufficient spatial frequency in the XY plane to cause substantial light scattering. Here, 'mild' means that the height corrugation has to be comparable to or preferably smaller than the above-mentioned optimum spacer thickness (~100 nm). The expected light propagation and reflection in this extended tri-layer structure are schematically illustrated in Figure 3. It is assumed that the ~100 nm spacer does not offset the roughness of the reflector surface, so that a similar level of roughness persists at the spacer/absorber interface.

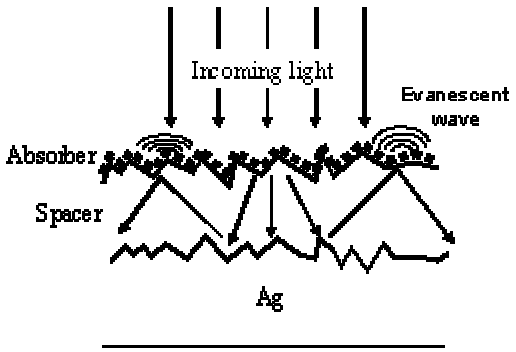

Figure 3 *Schematic illustration of how incoming light is scattered and reflected in a tri-layer structure with a diffuse-reflecting Ag mirror.*

In Figure 3, the incoming light is partially scattered by the roughness at the spacer/absorber interface, and the following reflection at the roughened Ag surface increases the average scattering angle and gives diffuse-reflected light back to the spacer/absorber interface. Some fraction of the thus diffuse-reflected light at relatively large angles then undergoes a total internal reflection at the absorber/spacer interface, thereby yielding a local evanescent wave in the absorber layer. This near-field can interact much more effectively with the absorber to increase its overall absorptivity. In addition, the total internal reflection at the spacer/absorber interface tends to confine the incoming light in the spacer region, thereby increasing the chance of the absorber to capture the multiply reflected light. Importantly, the basic function of the tri-layer structure, causing a maximum of ~5 times absorption enhancement by the constructive interference effect, as shown in Figure 2, still holds even in this extended version of tri-layer structure with a moderately diffuse-reflecting mirror surface. Thus the overall enhancement factor may easily exceed ~10 or higher.

Experimental

A vacuum-evaporated Ag film on a slide glass was used as the optically flat reflector in the standard tri-layer configuration. An Ag film DC-sputtered on glass, in the condition that the film under growth was heavily exposed to the Ar^+ ion plasma, gave the level of surface roughness to be ideal for the diffuse reflector in the proposed system. The transparent dielectric spacers with various thicknesses were prepared by spin coating commercial SOG (spin on glass) solutions (diluted to match the required thickness) followed by heating on a hot plate at 200°C. A thin absorber layer was prepared by spin coating 0.1 w% aqueous solution of PVA containing 0.05 mM RhB (rhodamine B). The fluorescence was excited typically at 532 nm

Results and Discussion

Figure 4 compares typical fluorescence spectra from the thin RhB/PVA film directly coated on glass (*a*) and from that in the standard tri-layer structure with ~100 nm spacer (*b*). It can be seen that the fluorescence enhancement factor in this example amounted to ~15.

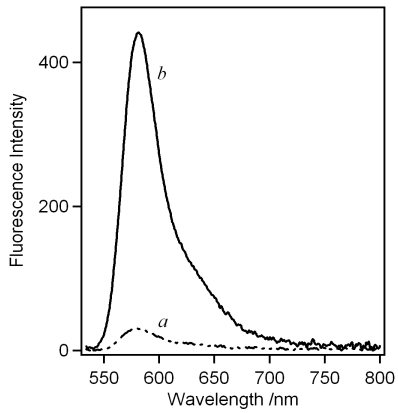

Figure 4 *Comparison of fluorescence spectra of thin RhB/PVA film on glass (a) and that in standard tri-layer structure (b) with 100 nm thick SOG spacer and an evaporated Ag film.*

Care should be taken however, because the fluorescence in the former case (on glass) is emitted both into the front space and into the backspace, while in the latter case (tri-layer structure) it is concentrated into the front space. Since the emission was detected in the front space at a fixed angle, the apparent fluorescence

intensity from the tri-layer structure is at least doubled even when the light absorption efficiency is equal. Correction for this and some other effects that influence the apparent fluorescence intensity leads to the conclusion that the net light absorption by the RhB absorber layer in the standard tri-layer structure was ~5 times as large as that on the glass surface, in agreement with the theoretical prediction as shown in Figure 2.

The crucial role of the spacer thickness in the tri-layer structure for the large fluorescence enhancement is demonstrated in Figure 5, where the peak fluorescence intensity is plotted as a function of the spacer thickness. A clear maximum was indeed observed with ~100 nm spacer thickness. The fluorescence intensity at spacer thickness far away from this optimum value on both sides becomes even lower than that obtained for the RhB/PVA layer directly coated on glass. For these spacer thicknesses, the interference between the incident and reflected (by the Ag mirror surface) light turns to be of destructive type.

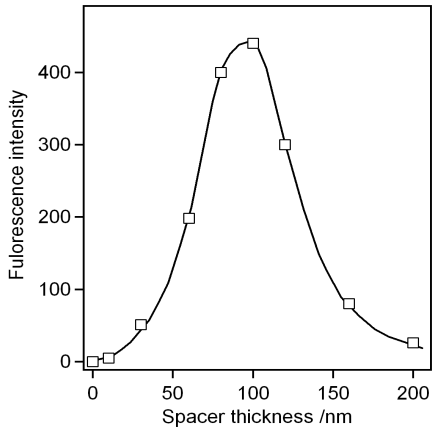

Figure 5 *Effect of spacer thickness on the RhB fluorescence intensity from the standard tri-layer structure*

As expected, the fluorescence enhancement as achieved with the modified tri-layer structure comprising a diffuse-reflecting Ag mirror was much higher than that given by the standard tri-layer structure; see Figure 6. Here, the corresponding fluorescence spectrum (*c*) is compared with those (*a* and *b*) already shown in Figure 4. When compared with the spectrum for the RhB absorber directly coated on glass surface, the enhancement factor amounts to ~45. Even if this is corrected for the aforementioned additional factors that apparently increase the fluorescence intensity detected in the front space, quite a large light absorption enhancement more than 10 times is of no doubt.

Figure 7 shows a roughness profile of the diffuse-reflecting Ag mirror, as measured by a stylus surface profilometer. The roughness profile little changed after coating of the 100 nm SOG spacer. Since the vertical resolution of the surface profilometer used here was limited to ~0.01 μm, the same order as the vertical corrugation observed in Figure 7, it is a little questionable whether Figure 7 represents a correct surface profile of the sample. However, the more important fact, which is obvious from Figure 7, is that the extent of the height corrugation is considerably smaller that the spacer thickness (~100 nm), in accordance with the model illustrated in Figure 3. It was confirmed that a tri-layer structure comprising a much rougher Ag mirror failed to give such a large fluorescence enhancement as demonstrated in Figure 6. Note, however, that the basic function of the tri-layer structure was still maintained even in such cases of highly roughened tri-layer structures.

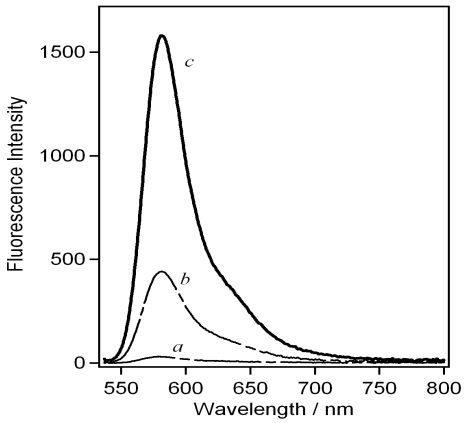

Figure 6 *Comparison of fluorescence spectra of thin RhB/PVA film on glass (a), that in standard tri-layer structure (b), and that in modified tri-layer structure with a diffuse-reflecting Ag mirror (c).*

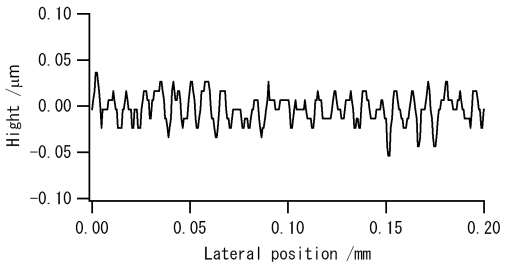

Figure 7 A surface profile of diffuse-reflecting Ag mirror surface.

References

[1] M. Kawasaki and S. Aoyama, Chem. Comm., pg. 988 (2004).

[2] M. Kawasaki and S. Aoyama, Proc. AgX2004, pg. 169. (2004)

[3] A. Bell and F. Spong, IEEE J. Quantum Electronics, 14, pg. 487 (1978)

Author Biography

Prof. Mitsuo Kawasaki graduated from Kyoto University in 1974. He received his Master of Engineering from Kyoto University in 1976, and a Doctor of Engineering from Kyoto University in 1985. He started working as an instructor at the Department of Industrial Chemistry, Kyoto University in 1978. He has been an associate professor at the Department of Molecular Engineering, Graduate School of Engineering, and Kyoto University since 1995. His current works are focused on the development of high efficiency photodevises based on nanoscale materials