

# Enhanced downconversion of UV light by resonant scattering of aluminum nanoparticles

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Metallic nanoparticles are known to enhance nonlinear optical processes due to a local enhancement of the optical field. This strategy has been proposed to enhance downconversion in thin film solar cells, but has various disadvantages, among which is the fact that the enhancement occurs only in a tiny volume close to the particles. We report on a very different physical mechanism that can lead to significant downconversion enhancement, namely, that of resonant light scattering, and which is a large volume effect. We show that only a tiny amount of resonantly scattering metallic (aluminum) nanoparticles is enough to create a significant enhancement of the fluorescence of dye molecules in the visible wavelength range. The strategy can be applied in general to increase the emission of UV-absorbing constituents, and is of particular use for solar energy. © 2012 Optical Society of America

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Enhancing the interaction of light with fluorescent molecules is of great interest nowadays owing to its importance for applications in many fields, including biosensing and solar energy. Metallic nanostructures offer an unprecedented opportunity to control light-matter interaction through their localized surface plasmon resonances (LSPRs), leading to huge enhancements of the near-field intensity and possibly to a strong light scattering [1]. It is well known that the radiative decay rate of a fluorescent molecule can be strongly modified in proximity to a metallic surface [2]. This typically occurs when the LSPR matches the emission band of the molecules [3]. An alternative approach consists of augmenting the amount of light absorbed by the molecules by matching the LSPR with their absorption band [4]. The latter approach is used, for instance, to increase the absorption efficiency of thin photovoltaic cells [5]. Now, while the large majority of studies in this framework are concerned with visible wavelengths (mostly using silver and gold as a material), several applications would benefit from enhanced light-matter interaction in the UV range. For example, aluminum (Al) nanoparticles (NPs), which are known to exhibit LSPRs in the UV range [6], have been used to improve the intrinsic fluorescence of proteins [7] and the light absorption in organic photovoltaic devices [8].

In this Letter, we report on a very different physical mechanism that can lead to a downconversion enhancement of light using metallic NPs. The strategy is based on the resonant light scattering by the NPs, which increases significantly the absorption of UV light, and thus enhance fluorescence away from their resonance wavelength, without disturbing the emission in the visible range. In particular, we show that a very low amount of Al NPs in a solution of UV-absorbing fluorescent molecules can be used for this purpose, which is the typical configura-

tion for dye-based downconversion in solar cells or luminescent solar concentrators [9]. The particular advantage of our strategy is that only a tiny amount of NPs are required to obtain a large enhancement, while maintaining a very good transparency in the entire visible wavelength range.

The system under consideration is shown in Fig. 1(a). It consists of a 2-mm-thick quartz cell containing a fluorescent solution absorbing UV light and emitting visible light through a downconversion process. Al NPs are dispersed in the solution to augment the absorption of UV light and, consequently, the fluorescence. The dye used in this study is 9,10-Diphenylanthracene (DPA). It absorbs UV light up to wavelengths of about 410 nm and

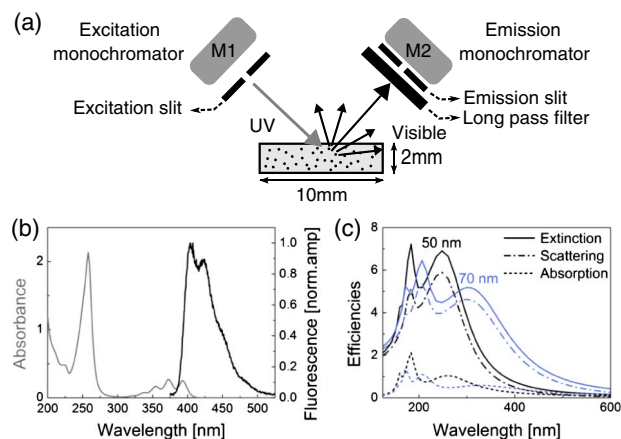


Fig. 1. (Color online) (a) Experimental configuration of the fluorescent solution (in light gray), absorbing UV light and emitting visible light, containing Al NPs (not to scale). (b) Absorption and emission spectra of DPA dissolved in acetonitrile. (c) Extinction properties of spherical Al NPs, calculated with Mie theory.

emits broadly from about 370 to about 530 nm [Fig. 1(b)]. The diameter of the Al NPs was determined such that their LSPR would overlap the absorption band of the molecules, yet without entering significantly the visible range. The scattering of light by spherical particles is well described by Mie theory, which provides exact analytical solutions of Maxwell's equations [10]. The extinction, scattering, and absorption efficiencies (ratios of the effective and geometrical cross sections) of a single Al NP (complex refractive index taken from [11]) of diameter 50 nm embedded in a medium of refractive index 1.35 are shown in Fig. 1(c). The Al NPs exhibit a strong LSPR with a maximal extinction overlapping well with the absorption band of the molecules in the UV range. Since Al NPs do not scatter much in the visible range, any additional effect of the NPs on the emission process can be avoided, while maintaining a good transparency of the fluorescent solution. It is also worth noting that the contribution of scattering in the extinction of Al NPs is much larger than that of absorption.

The samples were made according to the specifications given above. Spherical Al NPs of diameter ranging between 50 and 70 nm were purchased from IoLiTec GmbH. Al NPs are typically covered by an oxide layer of thickness from 2 to 5 nm, which causes a small redshift of the LSPR. A solution of dye was prepared by dissolving DPA in acetonitrile with a concentration of  $1.189 \times 10^{-4}$  M. Part of the solution was used for reference and the other to disperse the Al NPs. The dispersions were done by adding the Al NPs with a concentration of 0.01% in weight in the solution and sonicating it for 2 h at room temperature to disaggregate the NPs. A nonfluorescent dispersion of Al NPs in acetonitrile with the same concentration was realized following the same experimental procedures.

The absorption and extinction properties of the solutions containing the dye and the Al NPs, respectively, were characterized individually using a commercial UV-Vis spectrophotometer in transmission configuration. The extinction mean free path in the NP dispersion, obtained using the Beer-Lambert law, is shown in Fig. 2 and compared with the absorption mean free path of the solution containing the fluorescent molecules only.

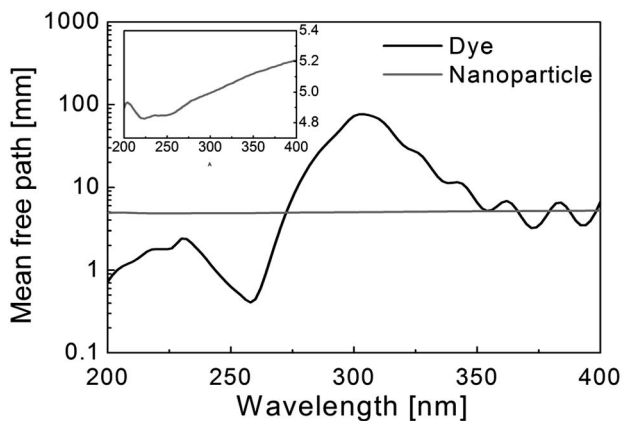


Fig. 2. Absorption mean free path of DPA dissolved in acetonitrile (black curve) and extinction mean free path of the Al NP dispersion (gray curve). Inset: close view of the extinction spectra of the NPs.

The extinction spectrum of the NP dispersion exhibits very weak resonant features over the entire UV range, yielding an extinction mean free path of about 5 mm in the range of 220–380 nm [see inset of Fig. 2]. This absence of features might be explained by considering the polydispersity of the Al NPs and the presence of NP aggregates in the solution [12]. First, the polydispersity in the NP diameter is expected to broaden the total extinction efficiency of the NP toward higher wavelengths [Fig. 1(c)]. The tail of the LSPR of 70 nm Al NPs clearly enters the visible region and is, therefore, expected also to affect the visible light transmission. Second, aggregates of resonant NPs (e.g., fractal aggregates [13]) are expected to scatter light on a broad range of wavelengths, yielding a rather featureless response in light scattering experiments. As a result, a ballistic transparency of about 68% at normal incidence on the 2-mm-thick solution was found in the visible range. A much higher transparency is expected for monodisperse and non-aggregated NPs.

The modification of fluorescence due to the introduction of Al NPs was investigated using a commercial fluorometer with excitation and emission monochromators, making it possible to select accurately the excitation and collection wavelengths. The quartz cuvette containing the fluorescent solution was mounted in front face illumination geometry in the fluorometer, light being incident at 45 deg with respect to the normal to the surface, and using a long pass filter to avoid detecting the light of the excitation [Fig. 1(a)]. Fluorescence measurements were characterized by exciting the samples at a particular wavelength and collecting the emitted light at all wavelengths. Figure 3 shows the fluorescence enhancement  $\gamma$  due to the addition of Al NPs as a function of the excitation wavelength. The fluorescence is shown to be enhanced at almost all wavelengths but those close to 260 nm, exceeding 20% in the range of 270–340 nm. The absence of fluorescence enhancement at wavelengths close to 260 nm is due to fact that the dye solution already absorbs most of the incident light, leaving no possibility to enhance it further by introducing the NPs. The enhancement of fluorescence for an excitation wavelength of 320 nm due to the addition of Al NPs in the luminescent solutions is evident in the inset of Fig. 3.

We now investigate the physical origin of the fluorescence enhancement reported above. The enhancement of absorption due to the presence of metallic NPs could first be attributed to the near-field intensity enhancement in the vicinity of the NPs. It can be calculated using an extended Mie theory generalized to absorbing host media [14]. For dilute dispersions of NPs, the overall absorption enhancement due to the near-field intensity enhancement can be estimated by considering the absorption enhancement in the average volume occupied by a single NP. Mie calculations show that the absorption enhancement expected for NP concentrations as low as 0.01% in weight (about 0.0029% in volume) would not exceed 1%. Although NP aggregates are expected to have somewhat different near-field intensity patterns, it is reasonable to state that near-field effects do not explain by themselves the fluorescence enhancement observed in our samples.

An alternative explanation for the absorption enhancement is the light scattering induced by the NPs. The

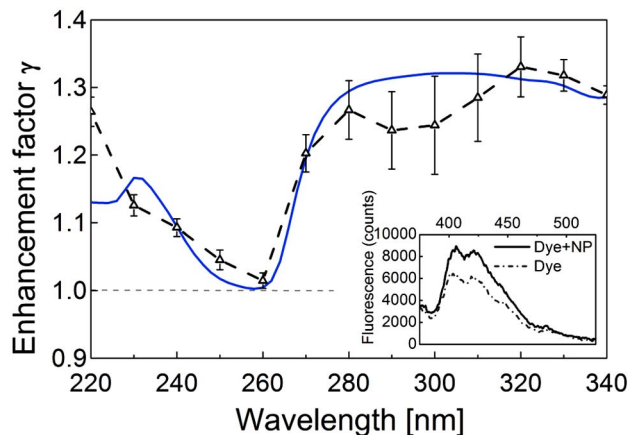


Fig. 3. (Color online) Enhancement factor  $\gamma$  versus the excitation wavelength (black triangles, dashed curve). The solid blue curve shows the enhancement expected from the light scattering model. The error bars were estimated from the intrinsic intensity fluctuations observed in the fluorescence spectra. Inset: fluorescence from the dye solution without Al NPs (gray dotted-dashed curve) and that with the Al NPs (black solid curve) for an excitation at 320 nm.

increase of light-matter interaction due to multiple scattering is a well-known phenomenon [15]. Multiply scattered light essentially spends more time interacting with the medium than ballistic light. In our case, we expect scattering to contribute the most to the extinction by the NP dispersion, in spite of the presence of NP aggregates in the solution. With a mean free path of about 5 mm for a cuvette of thickness 2 mm, light transport is clearly not diffusive, yet a single scattering event is already sufficient to increase the optical path length in the absorbing medium and, thus, increase the absorption of light by the medium. This hypothesis is verified by means of Monte Carlo simulations that model the transport of photons in scattering media [16]. Considering light incident at an angle of 45 deg on a medium with refractive index 1.35, thickness  $L = 2$  mm, scattering mean free path  $\ell_s = 5$  mm, and assuming isotropic scattering, we find the average optical path length to be  $\ell_{\text{eff}} = 3.12$  mm, compared with the path length in the bare slab  $l = 2.35$  mm. Knowing the absorption mean free path  $\ell_i$  in the dye solution (Fig. 2), the absorption enhancement due to scattering in the slab can simply be calculated as  $\gamma = (1 - \exp[-\ell_{\text{eff}}/\ell_i]) / (1 - \exp[-l/\ell_i])$ . Being in a weakly scattering regime at the emission wavelengths, the total amount of emitted light collected by the detector is expected to be proportional to the total amount of light absorbed by the medium. The resulting emission enhancement expected from light scattering effects, shown in Fig. 3, is found to be in excellent agreement with the

experimental results. The fluorescence enhancement remains higher than 20% at wavelengths above 270 nm and reaches 30%. It is clear from the expression of  $\gamma$  above that larger enhancements are expected when the intrinsic absorption of the dye is weak (i.e., large  $\ell_i$ ).

To conclude, we have reported on the fluorescence enhancement of solutions containing UV-absorbing molecules due to the addition of a very low concentration of Al NPs and shown that this effect was due to the light scattering by the Al NPs. This study offers a novel opportunity for enhanced light-matter interaction in the UV range with low interaction at visible wavelengths. The presented approach is general and may be applied to other metallic NPs exhibiting LSPRs at UV wavelengths. High fluorescence enhancements and transparency in the visible range are typically expected for monodisperse and nonaggregated NPs.

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## References

1. W. L. Barnes, A. Dereux, and T. W. Ebbesen, *Nature* **424**, 824 (2003).
2. C. D. Geddes and J. R. Lakowicz, *J. Fluoresc.* **12**, 121 (2002).
3. F. Tam, G. P. Goodrich, B. R. Johnson, and N. J. Halas, *Nano Lett.* **7**, 496 (2007).
4. O. Stranik, R. Nooney, C. McDonagh, and B. D. MacCraith, *Plasmonics* **2**, 15 (2007).
5. H. A. Atwater and A. Polman, *Nat. Mater.* **9**, 205 (2010).
6. P. R. West, S. Ishii, G. V. Naik, N. K. Emani, V. M. Shalaev, and A. Boltasseva, *Laser Photon. Rev.* **4**, 795 (2010).
7. M. H. Chowdhury, K. Ray, S. K. Gray, J. Pond, and J. R. Lakowicz, *Anal. Chem.* **81**, 1397 (2009).
8. V. Kochergin, L. Neely, C.-Y. Jao, and H. D. Robinson, *Appl. Phys. Lett.* **98**, 133305 (2011).
9. R. Renata, *Opt. Mater.* **32**, 850 (2010).
10. H. C. van de Hulst, *Light Scattering By Small Particles* (Dover, 1981).
11. E. D. Palik, *Handbook of Optical Constants of Solids* (Academic, 1985).
12. J. C. Weigle, C. C. Luhrs, C. K. Chen, W. L. Perry, J. T. Mang, M. B. Nemer, G. P. Lopez, and J. Phillips, *J. Phys. Chem. B* **108**, 18601 (2004).
13. V. A. Markel, V. M. Shalaev, E. B. Stechel, W. Kim, and R. L. Armstrong, *Phys. Rev. B* **53**, 2425 (1996).
14. I. W. Sudiarta and P. Chylek, *J. Opt. Soc. Am. A* **18**, 1275 (2001).
15. A. Ishimaru, *Wave Propagation and Scattering in Random Media* (Wiley-IEEE, 1999).
16. L. Wang, S. L. Jacques, and L. Zheng, *Comput. Methods Prog. Biomed.* **47**, 131 (1995).