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Fluorescence News

Luminescent Blinking from Noble-Metal Nanostructures: New Probes for Localization and Imaging

KEY WORDS: Silver and gold nanostructures; nanoparticles; luminescence blinking; enhanced photostability.

We have recently observed both one and multicolor luminescent blinking from a variety of noble-metal nanostructures upon laser-light illumination. Our results suggest a new class of metallic probes, based on intrinsic metal luminescence, with several advantages over conventional organic fluorophores such as enhanced photostability, higher luminescence intensity, tuneable emission wavelengths, and the possibilities for a variety of functional surface chemistries. Our findings for both silver and gold nanostructures have revealed some notable and attractive differences in their individual luminescence properties.

Silver nanostructures deposited on glass slides show a time-dependent activation and subsequent luminescent blinking, with multicolor blinking, differing in both intensity and location, also dependent on the type of structure and irradiance used. We have observed that silver fractal-like structures were highly emissive and could be photoactivated at a much lower irradiance, typically >30 W/cm^2, compared to glass-coated silver islands films and colloids, where silver island films were found to be the least emissive under similar experimental conditions, Fig. 1 [1]. At the onset of illumination, there was a rapid appearance of many highly emissive spots for all structures. The number of spots, observed using an Axiovert 135 TV Zeiss microscope in epifluorescence mode, increased for about a second and then remained constant. Most of the spots displayed blinking, which persisted during the many minutes of observation (Fig. 1, bottom). Some spots changed color as a function of time but did not photobleach, even after many weeks of study at high laser powers.

The luminescence properties of both silver and gold nanostructures appear to be notably different [2]. Firstly, much higher irradiances are required to observe gold-colloid luminescence, typically kW/cm^2. Second, although gold colloids have been observed to blink, no changes in foci color were seen, in contrast to the illuminated silver nanostructures. This interesting difference suggests the use of silver nanostructures as probes for multicolor applications.

The control of the nanoscale optical properties of silver nanostructures has led to nanophotonic devices ranging from nanosensors [3] to waveguides [4], as well as in a wide variety of applications in biotechnology [5,6]. Several recent publications have also reported luminescence from silver nanoparticles, particularly silver oxide particles, with envisaged applications in optical storage [7]. Although the nature of the luminescence is beyond the scope of this informative news article, recent microscopy studies of nanoscale silver oxide reveal strong photoactivated emission for excitation wavelengths shorter than 520 nm, with multicolor blinking, even from single nanoparticles. The individual luminescent species are thought to be silver nanostructures that are photochemically generated from the oxide [7], where several silver atom nanoclusters show a strong size-dependent luminescence [7]. To the best of our knowledge there have been no reports of gold luminescence.

APPLICATIONS AND ADVANTAGES OF BLINKING LUMINESCENT NANOSTRUCTURES

The widespread use of fluorescence as a tool in biotechnology has fueled the development of many new fluorescent probes. However, chemical stability, quantum

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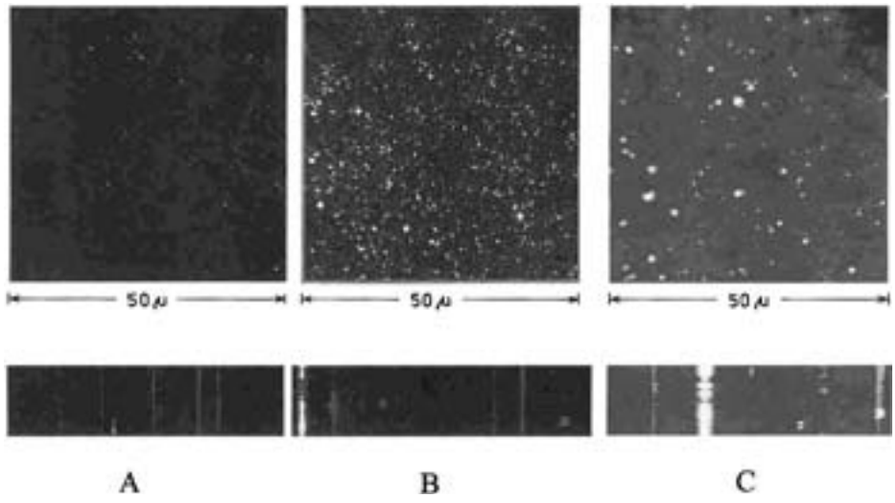

Fig. 1. Representative luminescence images of silver nanostructures on glass. A, Silver island films. B, Silver colloid–coated glass. C, Silver fractal coated glass. Intrinsic nanostructure luminescence was observed using the standard epifluorescence geometry of an Axiovert 135 TV inverted microscope with 442 nm HeCd 200 W/cm^2 excitation. For these images a water-immersion objective (40 × 1.2 NA) was used. Also shown (Bottom) are complied frames (200 ms/frame), which show the luminescent blinking of the silver nanostructures.

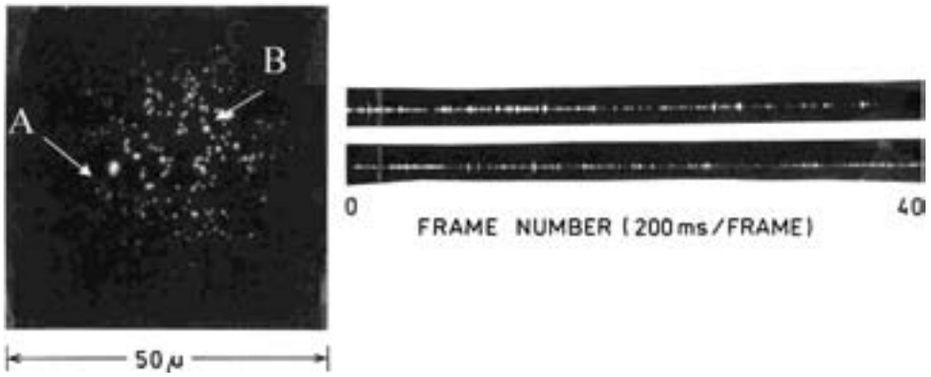

Fig. 2. Luminescence image of gold colloids spin-coated on a glass microscope slide upon excitation from a solid-state 532 nm, 5 kW/cm^2, frequency-doubled NdYAG. Also shown are the blinking traces for two luminescent foci, A and B.

yield, and the availability of reactive groups for further chemistries still hinders the practical use of many probes. The advantages of using silver and gold nanostructures as new metallic luminescent probes are likely to be many. Our findings have shown the metallic structures to be highly luminescent; they do not photodegrade over time (even at very high irradiances), and their surfaces can be readily functionalized using the many published properties of silver and gold [8–10]. In addition, their small size may allow their simple replacement with existing fluorophores.

These results suggest the use of emission from noble-metal nanostructures in nanophotoic devices and as luminescent probes for medical imaging.

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