Aluminum and copper nanostructures for luminescence enhancement / quenching

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Abstract

Metal enhanced/quenched luminescence was explored at the vicinity of aluminum and copper nanostructures. Ordered arrays of Al nano-islands with high aspect ratio were fabricated using nanosphere lithography combined with e-beam evaporation. Smaller-sized Cu nanoparticles (≤ 10 nm) were deposited on glass substrates using DC magnetron sputtering. Luminescence emission from Cy3 at the vicinity of these nanostructures was studied. Quenching of fluorescence was observed at the pure copper nanoparticle platforms. Signal manipulation of luminescent dye using Al and Cu nanoparticles will extend applications in different fields ranging from optoelectronics to biological research.

Introduction

Luminescence techniques have increasingly found promising applications in biological research including single molecule detection, cellular imaging, gene profiling, proteomics, drug discovery and disease diagnostic. Fluorescent markers are extensively being used for labeling for cell imaging. Signal weakness due to low concentration of fluorophores attached with molecules and low photostability of molecular fluorophores are two major concerns for this technique(*1*). Nearby conducting metallic particles, colloids, or surfaces are known to significantly influence the emission of vicinal luminophores [(2)]. Using nanoparticles platforms, it is possible to increase the quantum yield and photostability of weakly luminescent probes by increasing their emission efficiency, by modifying radiative decay rate or by coupling the emission with far field through scattering. Metal enhanced luminescence (MEL) has been studied mostly using silver and gold nanoparticles due to their intense, narrow SPR peaks. Gold nanoparticles are known to both quench and enhance luminescence depending on the fluorophore-particle separation distance, molecular dipole orientation with respect to particle surface and size of the nanoparticle (*3-5*). Relatively smaller (typically less than 30 nm) gold nanoparticles quench the fluorescence emission due to the non-radiative transfer from the excited states of luminophore molecules to the gold nanoparticles (*4*). Larger gold nanoparticles can enhance the luminescence due to the

increased contribution of nanoparticle scattering (*3, 6*). Enhanced signal and photostability of luminophores, improved surface immunoassay and DNA detection, and enhanced wavelength-ratiometric sensing, amplified assay detection are few examples of applications of MEL. On the other hand, quenching resulted due to metallic nanoparticles are successfully utilized for the improvement of homogeneous and competitive fluorescence immunoassay (*7, 8*), optical detection of DNA hybridization (*9*) , competitive hybridization assay (*10*) and in optoelectronics (*11*). The imaginary component of dielectric constant of copper is much larger (more than twice) than that of silver in the wavelength range of 300 nm to 600 nm. So, it is expected that in this wavelength range due to higher ohmic losses, Cu nanoparticles will mostly quench the luminescence at their close proximity (*12*). On the other hand, for large nanoparticles (>100nm) with high aspect ratios, MEL occurs mainly due to increase of the coupling efficiency of the fluorescence emission to the far field through nanoparticle scattering. In this case, as effect of ohmic losses on MEL is reduced, less expensive metals such as Al and Cu, which are more lossy than Ag and Au, can be considered as promising candidates for enhancing luminescence(*13*). This work focuses on the metal enhanced or quenched luminescence observed from aluminum and copper nanostructures.

Experimental Procedure

We created the single layer polystyrene nanosphere (Interfacial Dynamics Corporation, Portland, OR) mask by spin coating. Before coating, the glass substrates were cleaned in a plasma cleaner for 15 minutes. The nanospheres were obtained from the manufacturer as a suspension in water and were diluted using surfactant Triton X-100/methanol (1:400) before spin coating. The dilution factor for 400 nm nanospheres was 1:1. The Spin coating speed was 500 rpm for nanospheres. Al was deposited on nanospheres coated glass substrates using electron beam evaporation under high vacuum (2×10^{-6}) and Al deposition was followed by 10 nm of SiO_2 deposition. The SiO_2 layer was deposited on Al nanostructures to maintain a particular fluorophore nanostructure separation distance and to protect the Al film from oxidation. The thickness of film is measured with a quartz crystal microbalance. After deposition of metal, the polystyrene nanosphere mask was dissolved in ethanol by sonicating for 2 minutes. Copper nanoparticles were deposited on 22×22 mm glass cover slips (Fisher finest cover glass, thickness approximately 140 microns) using DC magnetron sputtering (Plasma Sciences CRC-100 Sputter Tool).

Cy3-streptavidin was first dispersed in 0.25% Poly (vinyl alcohol) (PVA, mw 15000) aqueous solution by sonicating. This fluorophore solution was coated on substrate by spin coating (3000

rpm speed). Surface morphology of nanosphere mask and nanostructures was observed by atomic force microscope (AFM) (Digital Instruments, Nanoscope IIIa). An UV- Vis spectrometer (JASCO, V-530) was used for measuring the light absorption spectra attributed to SPR of nanoparticles. The Leica DMI 4000b inverted fluorescence microscope equipped with Leica DFC340 FX CCD camera was utilized for MEL measurements. We obtained fluorescence intensities for each sample by analyzing a 1.64 mm× 2.19 mm image-section of each substrate.

Result & Discussion

Atomic force microscopy images of Al nanostructures indicate that it is not possible to obtain uniform nanosphere lithography over an area much larger than 10 micron using spin coating. Figure 1 (A) shows the AFM image of Al deposited on nanosphere lithographed glass slides. It can be seen that the image is comprised of two distinct areas 1) particulated thin film of Al where nanosphere coating was not present 2) isolated nanostructures of Al which was obtained from nanosphere coated area (Figure 1B). The interesting observation is that luminescence of Cy3 was observed to be enhanced significantly at the vicinity of Al nanostructured area where particulated thin film area does not show any enhancement (Figure 2). Cu nanoparticles quench (4.8 ± 2.48 times) the luminescence of Cy3.

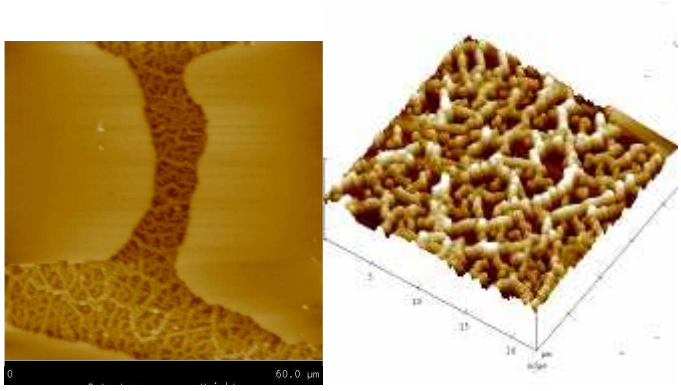

Figure 1:(A) AFM image of aluminum coated on glass substrate. (B) Isolated nanostructures of Al obtained from the nanosphere lithographed area

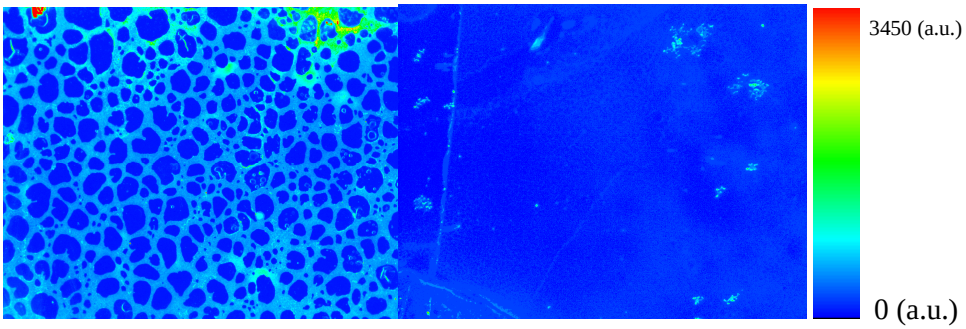

Figure 5: Pseudo colored image (intensity scale increases from blue to red) of Cy3 coated on (A) aluminum nanostructures (B) glass substrates.

The emission rate is increased due to the coupling of emission at far field through nanoparticle scattering. For large nanoparticles (>100 nm), effect of scattering is high and the effect of ohmic losses are not important (*15*). Hence, if scattering is high, even lossy metals such as Al and Cu can produce significant enhancements. This may be the reason why enhancement of Cy3 at the close proximity of Al nanostructures. On the other hand, since the Cu nanoparticles are of very small size (about 10 nm), we expect nanoparticle scattering to have less importance (*16*) so these nanoparticles result in quenching.

Conclusion

Using nanosphere lithography and E-beam evaporation we fabricated single-layers of larger (>100 nm) nanostructures of aluminum. Smaller sizes of copper nanoparticles were deposited using DC sputtering. We got promising results from preliminary study of fluorescence enhancement of Cy3 by Al nanostructures and fluorescence quenching by Cu nanoparticles. This finding opens new avenues for utilization of easily fabricated Al nanoparticles in MEL-based biological applications. We expect quenching effect of copper nanoparticles will motivate the utilization of these nanoparticles as less expensive alternative to gold in biological applications such as homogeneous and competitive fluorescence immunoassay, detection of DNA hybridization, competitive hybridization assay and in optoelectronics.

Acknowledgement

This study was funded by a grant from the National Science Foundation (No. CMS-409401). This funding is gratefully acknowledged.

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