Silver-copper alloy nanoparticles for metal enhanced luminescence

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Abstract

Silver-copper alloy nanoparticles were explored for metal enhanced luminescence (MEL) applications in this study. Surface plasmon resonance (SPR) wavelengths of these Ag-Cu nanoparticles were tuned in the visible and near infrared regions by changing annealing temperature. We observed strong emission enhancement of luminophores (141.48 ± 19.20 times for Alexa Fluor 488 and 23.91 ± 12.37 times for Alexa Fluor 594) when the SPR spectrum of Ag-Cu nanoparticles was tuned to result in maximum spectral overlap of the emission and absorption spectra of the luminophores with the SPR spectrum of the nanoparticles. This finding opens new avenues for utilization of metal alloy nanoparticles in MEL-based applications.

Introduction

Luminescence based measurements and devices are currently widely used methods in different fields such as biology, chemistry, materials science and medicine. Strong luminescence intensity is one of the most important desired properties for luminophores for these applications. It is possible to design and synthesis luminophores with desired spectral properties. The absorption and emission peaks of any luminophores can be predicted by analogy of known luminophores. But it is difficult to design luminophores with desired luminescence intensity. At the vicinity of conducting metallic nanoparticles such as those of silver and gold, the emission intensity of luminophores is known to be significantly influenced[1-4]. Using nanoparticles platform, it can be possible to increase the quantum yield of weakly luminescent probes by increasing it's emission efficiency by modifying radiative decay rate or by coupling the emission with surface plasmon resonance. It can also improve the intensity of luminophores that already have near unit quantum yield by enhancing their absorption by increasing the local field. Distance between the fluorophore molecules and nanostructured platform is also an important parameter in fluorescence enhancement[5]. Surface plasmon resonance (SPR) wavelength, one of the most important properties of nanostructures, dictates the choice of materials to be used for luminescence enhancement. Tam *et al.*[6] found that the enhancement is optimal when the plasmon resonance of the nanoparticles is tuned to the emission wavelength of the low quantum yield luminophores. Recently, some theoretical and experimental studies have suggested that luminescence enhancement is largest when emission wavelength is slightly red-shifted from the plasmon resonance[7,8]. One can expect that by tuning the position of the SPR peak of the nanoparticles over a wide range of wavelengths, metal enhanced luminescence (MEL) can be extended for a wide range of luminophores. Metal alloys offer additional degrees of freedom for tuning their optical properties by altering atomic composition and atomic arrangement. This motivates us to study alloy nanostructured platforms for MEL. Due to their interesting optical properties, we have chosen to study silver-copper alloy nanoparticles[9] for MEL application.

This work is focused on the use of alloy nanoparticles in the MEL. We demonstrate that SPR spectra of alloy nanoparticles can easily be tuned by manipulating only one experimental condition to result in maximum spectral overlap of the emission and absorption spectra of the luminophores with the SPR spectrum of the nanoparticles. We observed enhanced fluorescence emission from two thiol-reactive dyes, Alexa Fluor 594 and Alexa Fluor 488 (obtained from Molecular Probes, Invitrogen, Portland, OR), at the proximity of Ag-Cu alloy nanoparticles.

Experimental procedure

In this study, Ag or Ag-Cu nanoparticles were deposited on 22×22 mm glass cover slips (Fisher finest cover glass, thickness approximately 140 microns) by using DC magnetron sputtering (Plasma Sciences CRC-100 Sputter Tool). Before the depositions, the cover slips were cleaned by air plasma (Harrick PDC-32G) for 10 minutes at 6.8 watts power setting. During deposition, the background pressure was of the order of 10^{-6} Torr, the Ar pressure was 5 mTorr and the current was 25 mA. An Ag target was utilized to deposit the Ag nanoparticles and a Cu foil attached on the Ag target was utilized for the Ag-Cu nanoparticle deposition. Varying the ratio of the surface area of Ag to Cu exposed for sputtering allowed for changing the composition of the Ag-Cu alloy nanoparticles. Surface morphology of the nanostructures was observed and characterized by transmission electron microscopy (FEI Tecnai F20 S-Twin TEM). An electrical furnace (Lindberg, Blue M) was used for annealing of the Ag–Cu nanoparticles. Annealing temperature ranged from 298 K to 523 K and the annealing time was 5 minutes. Annealing was done in vacuum (30 inch Hg vacuum) to minimize oxidation of the nanoparticles. An UV-vis spectrometer (JASCO, V-530) was used for measuring the light absorption spectra attributed to the SPR of these nanoparticles.

Mouse Immunoglobulin G (IgG), labeled with luminophores Alexa Fluor 488 and Alexa Fluor 594 was coated on samples following known methods[2]. 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 and Discussion

Transmission electron microscopy of the Ag-Cu alloy nanoparticles indicated the average size to be 7.03 nm ± 1.97 nm (derived from a population of 100 particles) (Figure 1). The absorption spectra attributed to SPR of Ag-Cu nanoparticles show a single peak in the visible range. With increasing copper percentage, this SPR peak shifts to higher wavelengths and becomes broader (data are not shown here). This result confirms that the nanoparticles are bimetallic form of silver and copper and not a mixture of silver nanoparticles and copper nanoparticles[10]. The SPR peak of Ag-Cu alloy nanoparticles blue shifts upon increasing the annealing temperature from 298 K to 523 K (Figure 2). With increase in annealing temperature, Cu atoms surface-segregate, thereby increasing the concentration of Ag in the nanoparticle core. As a result, the conductivity of the nanoparticle increases[9,11] and the SPR peak shifts to lower wavelengths, as well as becomes narrower.

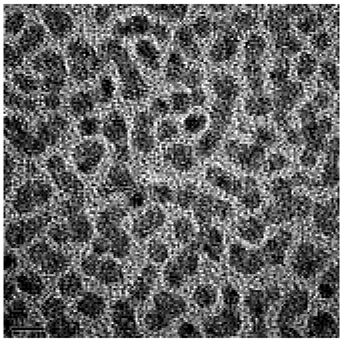

Figure 1: High resolution transmission electron micrograph of Ag-Cu alloy nanoparticles.

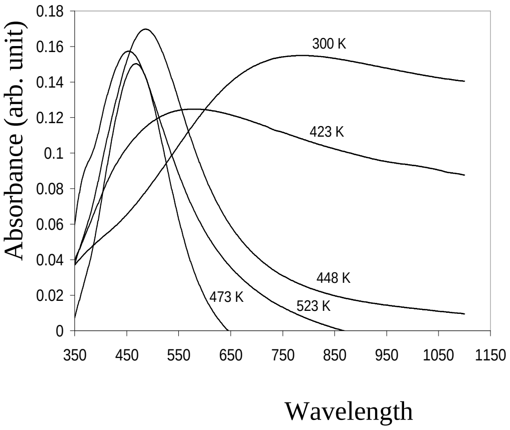

Figure 2. Absorption spectra of Annealed Ag-Cu nanoparticles

Luminescence of both Alexa Fluor 594 and Alexa Fluor 488 was observed to be enhanced significantly at the vicinity of these Ag-Cu nanoparticles. Enhancement ratio was calculated by comparing luminescence intensity of the sample with the luminescence intensity of the luminophore coated on a glass cover slip. As shown in Figure 3, the SPR spectrum of the 448 K annealed Ag-Cu nanoparticles nicely overlaps both the excitation and emission spectra of Alexa Fluor 488. This annealed Ag-Cu nanoparticle platform results in very strong enhancement (141.48 ± 19.20 times) of luminescence of Alexa Fluor 488. The Ag-Cu nanoparticles at 298 K, which show less spectral overlap, also result in large enhancement (100.87 ± 10.21 times). The lowest enhancement (50.22 ± 10.80) was observed at the proximity of pure Ag nanoparticles (deposited at the same conditions as Ag-Cu nanoparticles), where the spectral overlap is least.

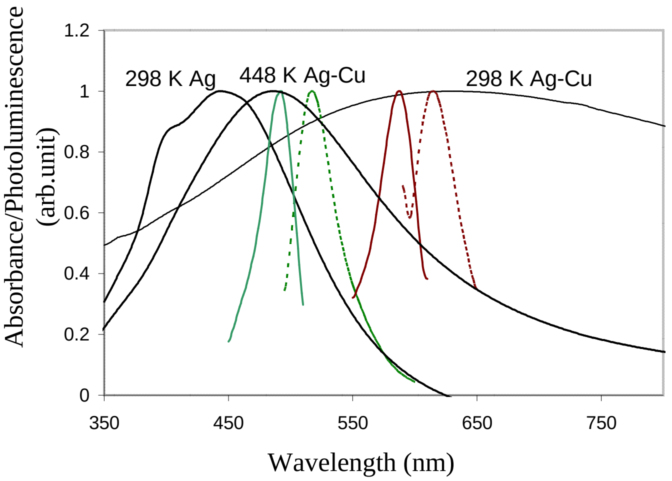

Figure 3. SPR spectrum of Ag-Cu nanoparticles and Ag nanoparticles used for MEL experiments and absorption and emission spectrum of Alexa Fluor 594 (----- emission spectrum, ____ excitation spectrum) and Alexa Fluor 488 (----- emission spectrum, ____ excitation spectrum). All spectra were normalized for comparison.

The effect of spectral overlap on luminescence enhancement is also pronounced for Alexafluor 594. We found 23.91 ± 12.37 times enhancement of emission from Alexa Fluor 594 at the proximity of room temperature grown Ag-Cu nanoparticles. On the other hand, both pure Ag nanoparticles and the 448 K annealed Ag-Cu nanoparticles grown at similar conditions result in lower enhancement (9.74 ± 0.9 times for 448 K annealed Ag-Cu nanoparticles and 6.89 ± 3.06

times for Ag particles) because of less spectral overlap. Luminescence enhancement is found to be a significant function of spectral overlap in this study.

Conclusion

SPR wavelengths of these Ag-Cu nanoparticles were tuned in the visible and near infrared region by changing only one experimental condition, annealing temperature. We observed strong emission enhancement of luminophores (141.48 ± 19.20 times for Alexa Fluor 488 and 23.91 ± 12.37 times for Alexa Fluor 594) at the vicinity of Ag-Cu nanoparticles when SPR spectrum was tuned to produce maximum spectral overlap. This study suggests that as SPR spectrum of Ag-Cu alloy nanoparticles can easily be tailored, this platform can be effectively used to enhance luminescence of different luminophores. This finding opens new avenue for the utilization of metal alloy nanoparticles in MEL applications.

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