



Short communication

Modified emission of polymer films by ultrathin Ag nanoparticle films

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ABSTRACT

Thin nanoparticle films with tunable and broad surface plasmonic absorption were obtained by disintegrating Ag films upon thermal annealing. The Ag thin film deposited by Physical Vapor Deposition (PVD) system was turned into the Ag particle film after annealing. The Ag particle films can be used as an enhanced fluorescence substrate. In this work, the emission of polymer films at 620 nm was tuned by the Ag particle films we prepared. The enhancement of fluorescence depends on the distribution of the particle films, i.e. the size of particles and the distance between particles. The maximum enhancement of fluorescence was nearly 9 folds. We attributed the enhancement of fluorescence to the enhanced local field induced by the Local surface plasmon resonance (LSPR) of nanoparticles. The local field in presence of Ag nanoparticles was calculated by using the finite-difference-time-domain (FDTD) method, the theoretical results agreed with the experimental results.

Nano-materials such as Ag or Au nanoparticles and nanostructured films exhibit unique optical properties due to the local surface plasmon resonances (LSPR) effect [1] and have attracted great interests in many fields, such as Surface Enhanced Raman Spectroscopy (SERS), Metal Enhanced Fluorescence (MEF) [2], optical devices [3], nano-waveguides, chemical and biological sensors [4], photovoltaics [5], and nanosensing [6] and so on [7–11]. However, the applications of metallic nanoparticles continue to face many problems, such as the stability and distribution of nanoparticles limit their practical applications. Thin metal film can disintegrate into nanoparticles upon thermal annealing. Tailoring the agglomeration behavior of thin metal films is a feasible way to prepare nanoparticles with controlled size, shape and distribution, which is known to exhibit efficient enhancement to the emission of luminescence centers from nearby fluorophores [12–16].

In this work, we present a facile method to prepare the Ag nanoparticle films with tunable and broad local surface plasmonic absorption by performing thermal annealed Ag ultra-thin films agglomerate treatments. The fluorescence of polymers was tuned by the prepared Ag nanoparticle films. The different fluorescence enhancement at 620 nm was demonstrated. Nearly 9 times enhancement at 620 nm was obtained by using the Ag nanoparticle films.

The Ag thin films with thickness of ~ 10 nm were deposited by Physical Vapor Deposition (PVD) system. Annealing of the Ag films was performed in the vacuum drying oven. The temperature was raised to

200 °C and remained for different durations. The Ag films were changed into Ag nanoparticle films with different size and distribution after annealing. The morphologies of Ag nanoparticle films were obtained by atomic force microscope (AFM). The absorption spectra of the Ag nanoparticle films were taken with the UV-Visible-NIR Spectra-photometer.

Then the Ag nanoparticle films were covered by polymer of Su8 films doped with fluophor (Rhodamine 590 Chloride). The polymer films were deposited by spin coater with the rate of 3000 rpm. The thickness of the polymer doped Su8 layer was about 30 nm (measured by an Ambios XP-2 step Pro-filer). At last, the Su8 films were cured by soft baking (100 °C, 30 min). The emission spectra of the samples were obtained by Ocean Optics USB2000 + Spectrometer. The excited source is 532 nm continuous wave laser with a power of about 200 mW.

The enhanced electromagnetic fields in the vicinity of Ag nanoparticles were calculated by using the finite-difference-time-domain (FDTD) method. The simulation parameters were set based on the experimental results. The simulation calculations were made in 3 dimensions. The grid size was set to be 1 nm. The perfectly matched layer (PML) absorbing boundaries were used.

Fig. 1 shows the AFM images of Ag nanoparticle films, which have been annealed at 200 °C for different durations (a)40 min, (b)4 h, (c)6 h, (d)20 h. As shown in Fig. 1, the smooth thin film was translated to nanoparticle film after annealing. The nanoparticles are nearly

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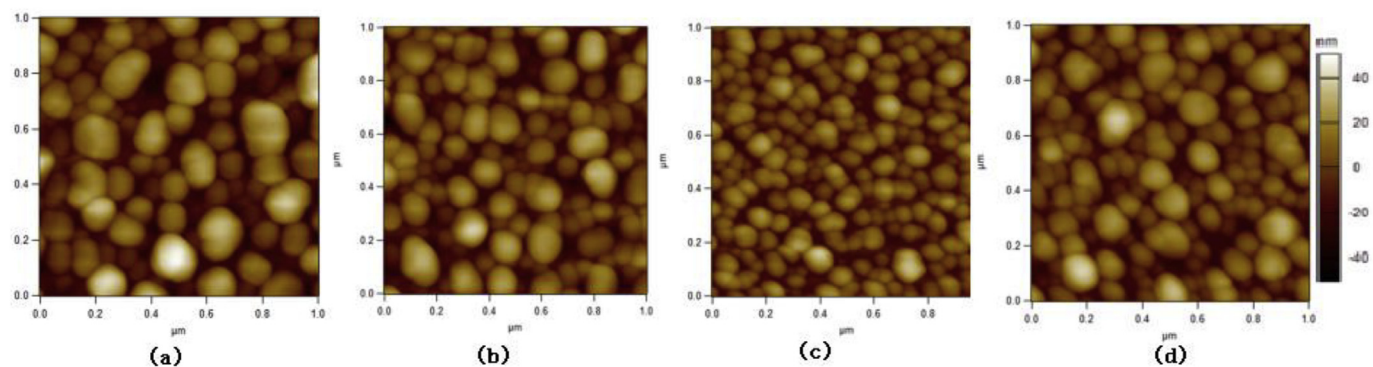


Fig. 1. The AFM images of the samples annealed at 200 °C for different durations. (a)40min, (b)4 h, (c)6 h, (d)20 h.

spherical. The sizes and spacing of nanoparticles depend on the annealing time. For the sample annealed for 40min in Fig. 1(a), the radii of the particles and the spacing between particles are large. Then the radii become smaller and the spacing decrease with the increasing of the annealing time, as shown in Fig. 1(b) and (c). The radii and the spacing of nanoparticles become large again in Fig. 1(d) with the further increasing of the annealing time. The results reveal that the annealing time is an important determinant for surface morphologies of Ag nanoparticles.

Fig. 2 shows the absorption spectra of Ag nanoparticle films. Ref. is the absorption of the thin Ag film, which was not annealed. As shown in Fig. 2, there is no obviously absorption band for the thin Ag film. When the thin Ag films are translated into Ag nanoparticles film, the broad absorption bands ranging from 400 nm to 550 nm are obtained. For the different nanoparticle films, the peaks of absorption bands are located at different wavelengths from 419 nm to 445 nm. The absorption bands of nanoparticle films come from the LSPR of nanoparticles, which mainly depend on particle size, shape, and aggregation condition of particles [15,17]. And the position of peak shifts towards longer wavelength with the increasing of particles sizes, which demonstrates that the absorption resonance band mainly depends on particle sizes in this work. We attribute the broad absorption bands to the efficient plasmon coupling among the neighboring Ag particles [18].

Then the Ag nanoparticle films were applied to enhancing fluorescence. The prepared Ag nanoparticle films were covered by Rhodamine 590 Chloride doped polymer films. The emission spectra of samples in presence of Ag nanoparticle films are shown in Fig. 3, which are recorded in the range from 550 nm to 700 nm under the excitation of

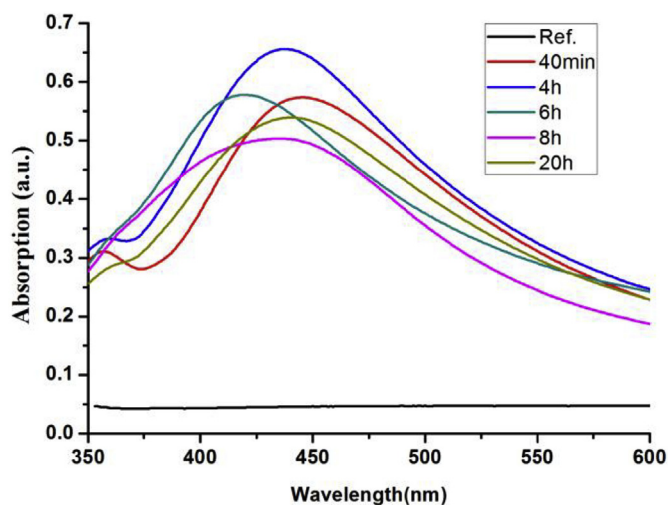


Fig. 2. The absorption spectra of Ag nanoparticle films, which are annealed for different durations.

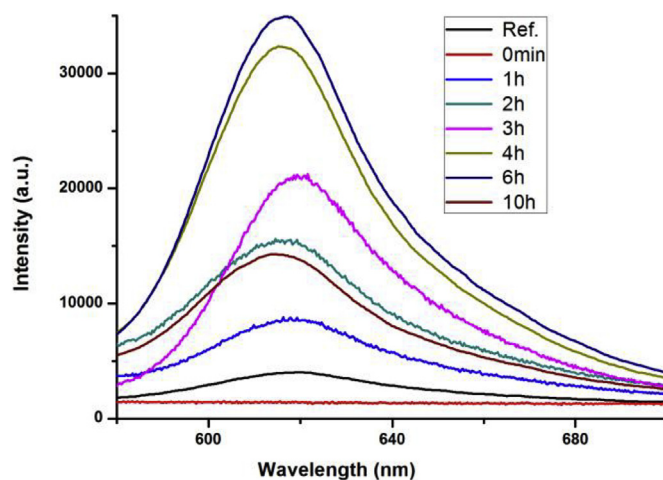


Fig. 3. The fluorescence spectra of fluorescence in presence of Ag nanoparticle films annealed for different durations.

532 nm laser. As shown in Fig. 3, the emission spectrum of isolated polymer film indicates a maximum emission at about 620 nm. For the sample in presence of Ag thin film, the emission is quenched. Then the emission is enhanced for the samples in presence of Ag nanoparticle films. The enhancement of fluorescence is different for the samples with different Ag nanoparticle films. Moreover, there is a slight blue shift of the emission peak due to the insertion of Ag nanoparticle films. Fig. 4 shows the corresponding enhancement factors (I_c/I_d). The I_c/I_b is the fluorescence intensity of polymers with and without Ag nanoparticles, respectively. According to Fig. 4, the fluorescence is quenched for the sample in the present of the Ag thin film, which is not annealed. We attribute the quenching to the energy transfer quenching [19]. After annealing, the Ag films convert into Ag nanoparticle films, the fluorescence is enhanced. The enhancement factor increases until reaching a maximum of about 9, then decreases again with the further increasing of the annealing time.

It is known that if the plasmonic nanoparticles present in the vicinity of the fluorophore molecules, the emission can be modified in two ways. One way is to increase the excitation rate by enhancing the local electric field, the other way is to change the radiative and nonradiative decay rates owing to the change of molecular density of states introduced by the LSPR effect [20,21]. Since the plasmon bands of Ag nanoparticle films from 400 nm to 550 nm close to the excitation wavelength at 532 nm, the nanoparticles and fluorophore form a coupled system, which mainly effects the excitation process rather than the emission process at 620 nm. This results in a higher excitation rate. So we attribute the enhancement of fluorescence to the increased excitation rates through local field amplification in presence of Ag nanoparticles. The slight blue shift of the emission peak is attributed to

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