Optical Materials 36 (2014) 1502–1505

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Light emission enhancement using randomly distributed plasmonic nanoparticle arrays

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ARTICLE INFO

Article history:
Received 2 October 2013
Received in revised form 10 March 2014
Accepted 4 April 2014
Available online 5 May 2014

Keywords:
Plasmonic array
Metallic nano-particles
Fluorescent dye

ABSTRACT

We have fabricated and characterised the optical properties of solution processed randomly distributed gold nanoparticle plasmonic arrays that are coated with a thin-film fluorescent dye. Three times enhancement in the emission intensity of the fluorescent dye Pyridine 2 has been observed. Our results are further supported by finite difference time domain simulations that predicted up to 7 times enhancements in the emission intensity as a result of the coupling between the molecular dipoles and the confined field in the underlying plasmonic array. Our results demonstrate the potential of using such structures in organic light emitting devices and chemical and bio-sensing applications.

1. Introduction

Localized surface plasmon resonances are collective non-propagating oscillations of conduction band electrons in metallic nanoparticles coupled into electromagnetic waves [1,2], that provide metallic nanoparticles with the ability to concentrate electromagnetic fields in sub wavelength volumes at the order of $(\lambda/15)^3$ [3]. These resonance frequencies can be adjusted through engineering the size and shape of the metallic nanoparticle [2,4]. There is significant interest in coupling semiconductor materials to such metallic nanoparticles, as they can be considered as an ideal system to study the fundamental physics of light matter interaction under extreme electromagnetic field confinement. Possible applications include quantum optics [5–7], light management [9–12] and chemical/biological sensing devices [8]. In particular the localized surface plasmon resonances for gold and silver have been extensively studied in systems designed for light absorption enhancement [9,10] with high interest for their applications in areas such as solar power harvesting [11] and enhancement of spontaneous emission rate [12].

Periodic plasmonic nanoparticle arrays are currently being extensively studied and used in designed plasmonic systems for the use in semiconductor photovoltaic and photonic systems due to their high potential in improving device efficiency in terms of absorption [11] and spontaneous emission enhancement [13–17]. Depending on the geometrical parameters of the plasmonic nanoparticle array and the optical properties of the emitting material in use, enhancements in the spontaneous emission intensity range between 3.6 and 83 have been already achieved [13,14]. Although periodic plasmonic system effectiveness was proven, the production of such structures is a relatively slow and costly process with a real difficulty in applying nano-scale lithographic patterning methods into real large-area devices. Thermally evaporated particulate metallic films are also extensively used to enhance the emission intensity of semiconductor materials with enhancements in the range 2–22 times already achieved [18–23]. However, vacuum thermal evaporation technique is costly, poorly scalable process and not always easy to incorporate particulate metallic films into the device layers [24–26]. On the contrary to the above two approaches, solution processed randomly distributed plasmonic nanoparticle arrays manufacturing is more efficient in terms of price and production time with the ability to be applied into real large-area devices using techniques such as roll-to-roll or inkjet printing. Despite these facts they are much less studied compared to the periodical arrays or thermally evaporated particulate metallic films. Just recently Xiao et al. [27] have shown that surface plasmon induced enhancement of electroluminescence by around ~25% in organic light emitting diode (OLED) with gold nanoparticle array embedded into the hole injection layer compared to 22–28% in OLED implementing 1D and 2D periodic plasmonic arrays [28] respectively.

In this paper we present the fabrication of solution processed randomly distributed plasmonic nanoparticle arrays and demonstrate over three times enhancement in the spontaneous emission

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http://dx.doi.org/10.1016/j.optmat.2014.04.010
0925-3467/

intensity of the fluorescent molecular dye Pyridine 2 by coupling the molecular dipoles into the confined optical field of the plasmonic nanoparticle array. Using three dimensional finite difference time domain (FDTD) calculations [29] we show that the emission intensity enhancements are strongly dependent on the gold fill factor (FF) with emission enhancement as high as 7 times being anticipated in structures have a FF of 0.4.

2. Experimental method

The structure we have fabricated and tested in this work is shown schematically in Fig. 1. The gold random plasmonic nanoparticle arrays were prepared through 1:1 ratio mixing of 0.05 mg ml^{-1} water suspended of 20 nm gold nano-particles (PlasmaChem GmbH) with polyvinyl alcohol (PVA) water solution at a concentration of 34 mg ml^{-1} then spin-cast onto a glass substrate to form a film of 30 nm thickness. The active layer was prepared by doping the molecular laser dye Pyridine 2 at a concentration of 0.5 mg ml^{-1} into ethanol solution containing the polymer poly (methacrylic acid) (PMA) at a concentration of 9 mg ml^{-1} then spin-cast onto the plasmonic array to form a film of 10 nm thickness.

Fluorescence spectra were measured using far field spectroscopy. Dark field excitation was provided using 405 nm with excitation density ~200 W cm^{-2}. Emission was collected at normal incidence from the sample surface using a 0.26 numerical aperture objective lens and directed toward a 0.25 m nitrogen-cooled charge-coupled device (CCD).

3. Results and discussion

Fig. 2(a) shows an AFM image of a 20 nm gold nanoparticle plasmonic array embedded in 30 nm PVA thick layer. As can be seen in Fig. 2(a) and (b) the gold nanoparticles are randomly distributed on the PVA surface with tendency to form clusters on a small scale. From Fig. 2(a) it is clear that some of the gold nanoparticles penetrate over the PVA surface. It is important to note that the AFM image only shows the particles distribution at the topmost surface that in a direct contact with the Pyridine 2/PMA layer. From the AFM results in Fig. 2(a) it is clear that the gold nano-particles have a random distribution in the vertical direction of the PVA layer.

Fig. 3(a) shows the emission spectra of Pyridine 2 measured from three different locations on the plasmonic array surface. The variation in the integrated emission intensity between these three different locations is less than 10%, illustrating that the gold

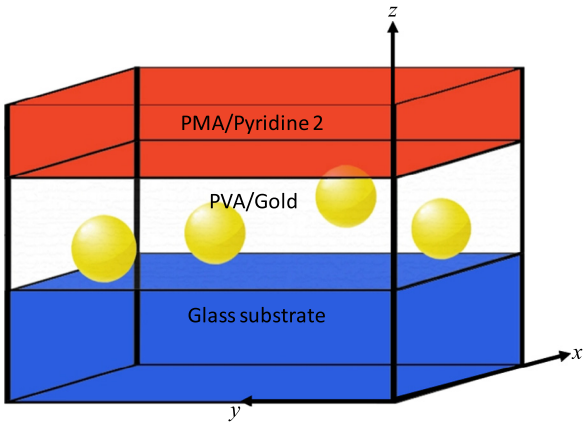

Fig. 1. Schematic drawing of the plasmonic nanoparticle arrays investigated in this work.

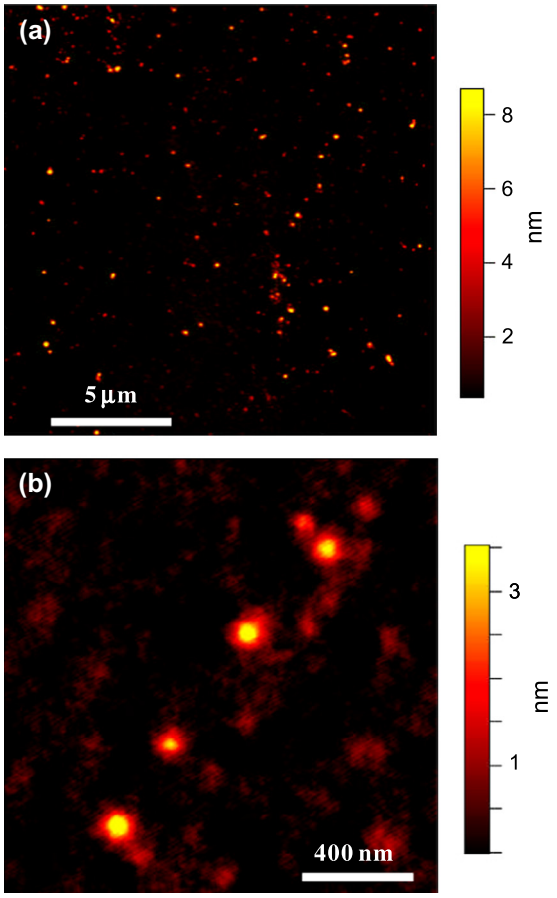

Fig. 2. (a) AFM image of plasmonic nanoparticle array. (b) High magnification image of a cluster region on the plasmonic array surface.

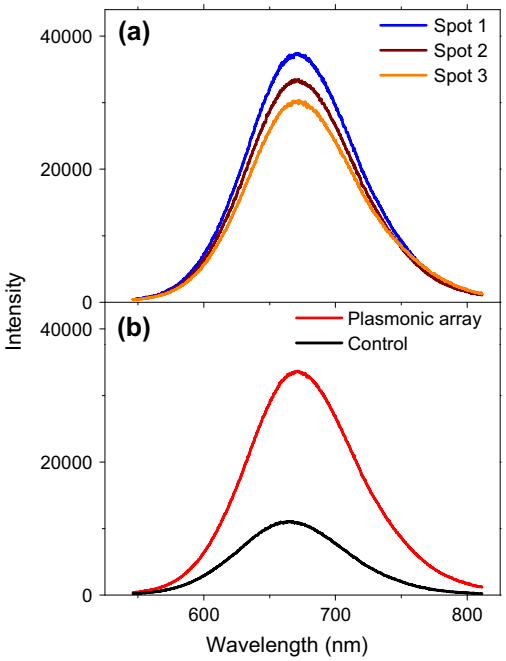

Fig. 3. (a) Fluorescence emission spectra of Pyridine 2 measured from three different locations on the plasmonic array surface. (b) Fluorescence emission of a control film of the molecular dye Pyridine 2 in PMA (black curve) together with the fluorescence emission of the Pyridine 2 when coated onto the plasmonic array surface.