Fluorescence emission enhanced by surface electromagnetic waves on one-dimensional photonic crystals

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An appreciable increase in the fluorescence emission of an organic chromofore is obtained by exploiting the local field enhancement at the surface of one-dimensional photonic crystals after excitation of surface electromagnetic waves (SEW). Using a properly designed photonic crystal consisting of alternating a-$Si_{1-x}N_x$:H layers with different nitrogen content, efficient emission of R6G dye spun on the surface of the photonic crystal is detected and the intensity spatial distribution of the SEW is visualized by means of far-field fluorescence microscopy. Our results demonstrate potential applications in enhanced fluorescence microscopy with an increased sensitivity and spectral selectivity. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3148671]

Semi-infinite photonic crystals (PC) can support surface modes propagating along the PC-vacuum interface.[1–3] Such surface modes are characterized by decaying fields in the perpendicular direction from the surface plane. Inside the PC the fields decay because of interference effects. Thus, the surface electromagnetic waves (SEW) in PCs have a different origin than surface plasmon-polaritons in a homogeneous semi-infinite metals since in the latter case the decay in the medium is caused by the negative dielectric function. SEW in one-dimensional photonic crystals (1D PC) are attracting continuous interest as an alternative to surface plasmons.[4] SEW on 1D PC present several advantages as compared to surface plasmons. For instance, 1D PC can be fabricated to provide SEW excitation in a broad wavelength interval ranging from the IR to the near-UV, depending on the materials and the specific design of the photonic structures. In addition, the low losses in 1D PC consisting of dielectric media provide the possibility of strong coupling between SEW and incoming light.[5] Strong coupling may result in higher intensity of SEW and leads to a much sharper resonance dips as observed, for instance, in prism reflectance spectroscopy.[6] This particular feature makes SEW-based sensors particularly attractive.[7–9]

In this work, the fluorescence emitted by a thin layer of organic dyes spun on the free surface of a 1D PC after excitation of SEW in the Kretschmann configuration is studied. The motivation of this work is to provide an experimental demonstration of the enhancement of the fluorescence emission out of the structure. It is shown that fluorescence is a suitable way for imaging the SEW spatial distribution by conventional far-field microscopy. The use of fluorescence enhanced by confinement of light at the surface of periodic planar structures[10] represents a promising detection channel for sensing and imaging applications [such as total internal reflection fluorescence (TIRF) microscopy[11]] in material science and biology. Here we show that the strong localization of the excitation radiation close to the surface significantly enhances the dye thin-layer fluorescence intensity with a consequent increase in fluorescence bleaching. Advancing the idea of fluorescence enhancement at the surface of PC recently proposed in Ref. 10, we managed to directly map the 2D distribution of both the SEW field and emitted fluorescence intensities and highlight the connection between SEW coupling and fluorescence enhancement. This allows a comprehensive analysis of SEW parameters such as propagation length and bleaching kinetics.

1D PC based on hydrogenated amorphous silicon nitride (a-$Si_{1-x}N_x$:H) are synthesized growing stratified structures by 13.56 MHz plasma-enhanced chemical vapor deposition on glass coverslips. Depending on the nitrogen content, a-$Si_{1-x}N_x$:H can have a tunable refractive index and optical gaps over a wide energy range.[12] The composition of the a-$Si_{1-x}N_x$:H layers was controlled by operating on the ammonia fraction in a SiH_4+NH_3 plasma.[13] Careful analysis based on transmittance reflectance spectroscopy performed on single layers and multilayer structures and fitting procedures based on transfer matrix method provided the right feedback to the deposition conditions such as ammonia/silane gas fraction and deposition times. Thus, stacked structures with a good control of the optical thickness for each single layers has been obtained. The 1D PC used in this study consists of 15 pairs of a-$Si_{1-x}N_x$:H layers. Layers with high ($n_H=1.99$ at $\lambda=532$ nm) and low ($n_L=1.72$ at $\lambda=532$ nm) refractive index have thicknesses of $d_H=60$ nm and $d_L=125$ nm, respectively. The structure is terminated at the air side with a low-index layer. The sample is optically contacted with a BK7-glass prism in the Kretschmann–Raether configuration.

Experimentally, SEW is coupled using a slightly focused TE-polarized frequency-doubled neodymium doped yttrium aluminum garnet laser beam at $\lambda=532$ nm illuminating the sample through a 45° BK7-glass prism providing the coupling beyond the light line at the glass/air interface. A microscope mounting a 10× objective with a low numerical aperture (NA=0.2) collects the light emitted from the 1D PC/air interface in the free space, in accordance with the sketch

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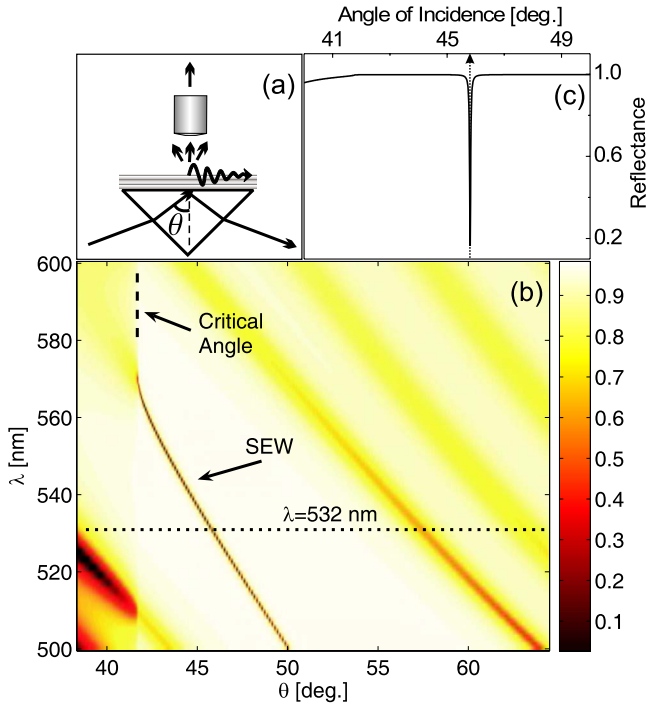

FIG. 1. (Color online) (a) Schematic of the Kretschmann configuration for the SEW coupling and detection. (b) Calculated normalized reflectivity map $R(\theta,\lambda)$ of the 1D PC illuminated in the Kretschmann configuration. Darker regions indicate lower reflectance. SEW dispersion curve is indicated by the arrow. (c) Calculated reflectivity angular spectrum for the 1D PC grown optimized for the 532 nm excitation of SEW. The excitation wavelength is 532 nm. The coupling angle θ is marked with an arrow and estimated as ~46°.

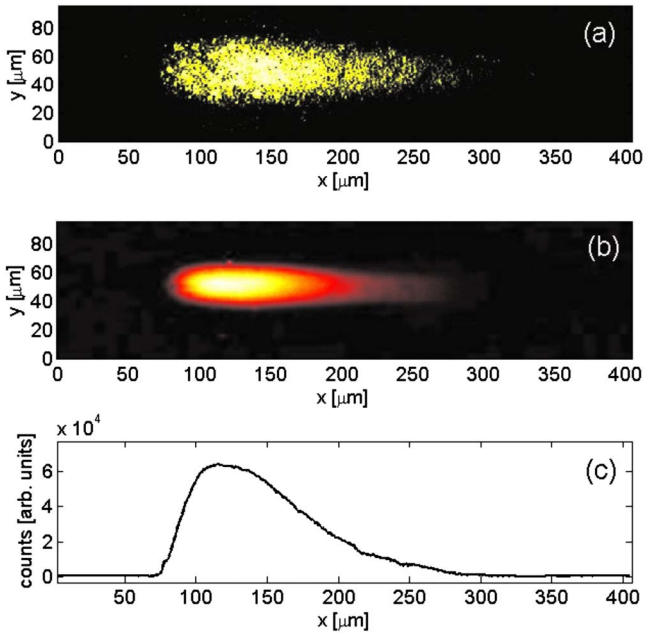

FIG. 2. (Color online) SEW spatial distribution imaged by collecting (a) the light scattered by microdefects on the 1D PC surface and (b) the fluorescence emitted by organic dyes on the 1D PC surface. (c) Fluorescence intensity profile along the SEW propagation direction.

depicted in Fig. 1(a). The small NA objective ensures a wide field of view. Figure 1(b) shows calculated reflectivity response of the considered 1D PC when prism-illuminated by a plane wave impinging on the internal glass/1D PC interface at an angle θ and a wavelength λ. A color map in the (θ,λ) plane shows high and low reflectivity regions in the wavelength range from 500 to 600 nm. SEW dispersion curve appears as the low reflectivity, narrow dark band beyond the air light line, located inside the first photonic forbidden band. As soon as the SEW dispersion curve crosses the air light line (corresponding to the critical angle for which the TIRF occurs), it becomes extremely broader till it disappears. In such a situation, the mode is no more bounded to the surface and becomes leaky on both the multilayer and the air side. The coupling angle is estimated from the position of the narrow dip corresponding to SEW excitation calculated for 532 nm of excitation wavelength as shown in Fig. 1(c).

Observations and spectral measurements are conducted by means of a fluorescence microscope coupled to a grating-based spectrometer after a low-pass filtering with cutoff wavelength at 545 nm. This allows acquisition of both fluorescence wide-field images and fluorescence spectra from the sample surface. Rhodamine 6G dye is used as fluorescence emitter. An ethanol solution of Rhodamine (10^{-5} molar concentration) was spun at the surface of PC and dried at ambient conditions. The dye film thickness is estimated to be in the interval between 100 and 150 nm. When coupling SEW, the slight shift of the SEW dispersion curve toward larger coupling angles due to the organic dye film is taken to account.[6] False-color representations of measured far-field microimages of SEW are shown in Fig. 2.

When the SEW is excited, part of the incident radiation is rescattered out-of-plane and detected by the microscope objective. As it is possible to appreciate from Fig. 2(a), the main source of scattering is provided by the microdefects at the sample surface. The SEW is spatially distributed in a cometlike pattern strongly elongated in the propagation direction. We evidence the SEW propagation length of approximately 200 μm that is at least in four times larger than the surface plasmon length on gold films in the visible range [Fig. 2(c)]. Depending on the coupling conditions, the SEW propagation length can be varied.[5] When the 545 nm cutoff filter is applied, the laser radiation is blocked and a fluorescence image of the SEW is obtained. The fluorescence image shown in Fig. 2(b) has the same form and size as that of the SEW image but appears to be smoother as compared to the scattered field. In fact, no significant changes in fluorescence emission are observed corresponding to the microdefects, meaning that the scattered light does not significantly contribute to the fluorescence excitation as the SEW near-field does. This effect suggests that a proper use of fluorescent emitter might represent a more reliable way for SEW detection as compared to the resonant elastic scattering out of plane.

Due to the focalization of the illuminating beam, the SEW is rather weakly coupled in this case. In a previous work,[5] a strong field enhancement is shown to be produced at the 1D PC surface once SEW are coupled. Here, we demonstrate that such an enhancement can be further exploited for boosting the fluorescence emission. We underline that the beam divergence plays a crucial role in the field enhancement effect. If the beam is well collimated, the coupling strength is larger and the SEW intensity is higher.

The fluorescent enhancement can be estimated from the spectra shown in Fig. 3. The solid line represents a spectrum measured in center region of the SEW excited by the TE-polarized laser beam. The reference spectrum shown by dot

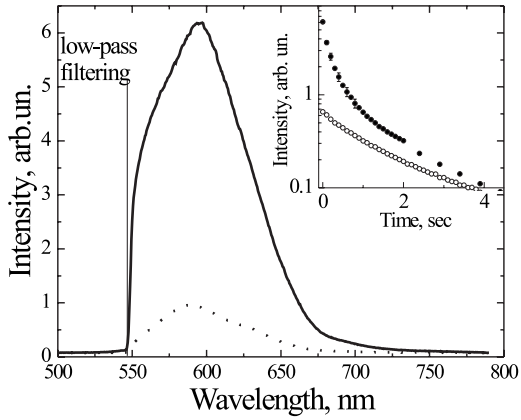

FIG. 3. Fluorescence spectra of Rhodamine 6G on the surface of 1D PC for TE (solid line) and TM (dot line) polarization of the incident light. SEW is only coupled for a TE-polarized incident light. Inset. Time variations of the fluorescence intensity measured at $\lambda = 590$ nm for TE (filled circles) and TM (open circles) polarized laser excitation caused by the dye molecules photobleaching.

line in Fig. 3 is measured over the same area as the illumination laser beam is TM-polarized that ensures the absence of the SEW coupling. Polarization is varied by means of a fiber-based polarization control, therefore the intensity of the beam in both linear polarization states is almost identical. Both spectra are peaked at approximately 590 nm and an enhancement of fluorescence intensity corresponding to SEW coupling is about six times in magnitude. Here, the illumination divergence was optimized for a weakly coupled SEW, in such a way that the field spatial distribution of the mode could be visualized. By using collimated beams, the enhancement can be further increased,[5] thus leading to a uniform field distribution over wide areas that can be fruitfully exploited in TIRF microscopy. The shape of the emission spectrum is only slightly affected by the presence of the photonic structure beneath the emitter layer. Nevertheless, in an eventual TIRF setup, particular attention must be paid to the effects of a spatially inhomogeneous SEW redshift as a consequence of the thickness and refractive index inhomogeneities of the bioassay placed on the 1D PC surface. Such a feature could be exploited yielding high-contrast fluorescence imaging related to the specific specimen morphology. The enhancement of fluorescence excitation, induced by the SEW mode coupling, is evidenced also by a rapid bleaching of the Rhodamine 6G dye[14] as highlighted in the inset of Fig. 3.

In conclusion, the Rhodamine 6G fluorescence intensity enhancement due to the SEW coupled on surface of 1D PCs is observed. Fluorescence-mediated SEW distribution is visualized by means of far-field fluorescence microscopy. Spectral tunability of the SEW excitation depending on the effective PC dispersion can be finely controlled by specific structure designs in addition to the intrinsic material dispersions, thus opening prospectives for the application of SEW-enhanced fluorescence microscopy in biosensing with an increased concentration sensitivity and spectral selectivity.

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