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## Frequency conversion of propagating surface plasmon polaritons by organic molecules

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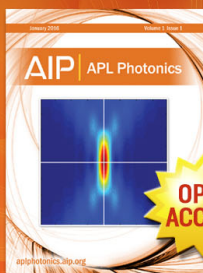
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## Frequency conversion of propagating surface plasmon polaritons by organic molecules

T. K. Hakala,<sup>1</sup> J. J. Toppari,<sup>1,a)</sup> M. Pettersson,<sup>2</sup> A. Kuzyk,<sup>1,3</sup> H. Tikkanen,<sup>2</sup> H. Kunttu,<sup>2</sup> and P. Törmä<sup>3</sup>

<sup>1</sup>Nanoscience Center, Department of Physics, P.O. Box 35, 40014 University of Jyväskylä, Finland

<sup>2</sup>Nanoscience Center, Department of Chemistry, P.O. Box 35, 40014 University of Jyväskylä, Finland

<sup>3</sup>Department of Engineering Physics, P.O. Box 5100, 02015 Helsinki University of Technology, Finland

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We demonstrate frequency conversion of surface plasmon polaritons (SPP) by utilizing the coupling between organic dye molecules and SPP. Launching of SPPs into a plasmonic waveguide is done in two ways: by optically excited molecules and by quantum dots (QDs). QDs are demonstrated to overcome the major problem of bleaching occurring with molecules. The SPP propagates tens of micrometers and clear frequency conversion is observed in the SPP spectrum after passing an area of converter molecules. The use of molecules and QDs as elements of all-plasmonic devices has the potential for high integration and use of self-assembly in fabrication. © 2008 American Institute of Physics. [DOI: 10.1063/1.2987726]

Surface plasmon polaritons (SPPs) are coupled excitations of electromagnetic field and free electrons in metal, which can propagate in a wavelike fashion along a metal-dielectric interface.<sup>1,2</sup> SPPs can also be confined to dimensions much smaller than the wavelength of light in free space. Thus SPPs may provide the path to integrated electrical and optical circuits in nanoscale. There has been substantial progress in recent years, for example, in guiding of SPPs in metallic structures<sup>3–6</sup> and realizing optical elements<sup>5–7</sup> or even in developing active devices.<sup>8–10</sup> The interaction of SPPs with molecules is also studied and utilized widely, e.g., in biosensors and in surface enhanced Raman scattering,<sup>11</sup> as well as in coupling of SPPs into far field in order to visualize them.<sup>7</sup> More recently, molecules have also been used to attenuate SPP propagation<sup>9</sup> and to couple light into SPP modes in planar structures,<sup>12</sup> as well as in plasmonic waveguides, thus realizing an energy transfer via propagating SPPs.<sup>13</sup> In this letter, we realize a frequency converter for propagating SPPs, an essential component in integrated plasmonics, by utilizing molecules. We build on the earlier demonstrations on coupling of SPP to far field light by molecules.<sup>7,9,11–13</sup> The key development here is the realization of an *all-plasmonic* device, i.e., SPP to SPP frequency conversion. The initial launching of SPPs is also done by molecules, and in addition, we show that quantum dots (QDs) can be used to launch SPPs and thus achieve a more stable source of SPPs than by molecules.

The operation principle of the frequency converter is shown schematically in Fig. 1. SPPs are launched into a microscale plasmon waveguide by a SPP source consisting of fluorescent Coumarine 30 (C30) molecules or, alternatively, QDs deposited at close proximity to the waveguide surface and excited by 405 nm laser light. The waveguide is a 5  $\mu\text{m}$  wide silver stripe of  $\sim 130$  nm thickness. The emerged SPPs have distinct spectra of the emitters used in the SPP source, i.e., maxima near  $\lambda=480$  nm for C30 (see Fig. 3) or  $\lambda=550$  nm (see Fig. 4) for QD, and they propagate along the waveguide reaching the area of the *converter*

*molecules*, Rhodamine 6G (R6G) for C30 or Sulforhodamine 101 (SR101) for QD. Since the emission spectrum of the SPP source overlaps with the absorption spectrum of the converter molecules, the latter is excited by the SPPs. Consequently, the converter molecule being excited is decaying nonradiatively via vibrational relaxation to the bottom of the electronic excited state, as shown in the inset of Fig. 1. This state can now decay by emitting free space light or couple back to the waveguide as a SPP. Since the molecules excited are those strongly coupled to SPPs, their relaxation probability to SPP should also be substantially larger than that to free space light.<sup>11</sup> The converted SPPs further propagate to the end of the waveguide. The edge of the waveguide serves as an efficient scattering center of SPPs to far field.

The waveguides were fabricated on the top of an indium tin oxide coated glass by e-beam lithography. The molecules were positioned on top of the waveguide by embedding them into negative SU-8 polymer resist (Microchem SU-8 2000 series), which was consequently spun and exposed by e-beam, leaving the exposed area on the chip.<sup>13</sup> The thickness of the SU-8 layer was 60 nm for C30 films and was varied between 100 and 430 nm in different experiments for both the R6G and SR101 films. In each experiment, such as the ones reported in Figs. 3 and 4, all the samples had the same SU-8 thickness within the fabrication accuracy of  $\sim 10$  nm. The QD SPP source was fabricated by e-beam lithography and lift-off technique by drying an aqueous QD solution onto the polymethyl methacrylate mask. In Fig. 2(a) the red circular area is the C30 region launching SPPs isotropically along the silver surface while excited. The sample has different waveguide configurations to four different directions, all fed by the same SPP source. These are needed to obtain reference data necessary to distinguish the signal due to SPPs from the far field background.

The optical measurements were carried out in a confocal microscope (Olympus Fluoview-1000) equipped with a dual scanner and a 100 $\times$  air objective (numerical aperture = 0.95) used for excitation and collection. Photomultiplier tubes (Hamamatsu R6357) with a flat frequency response within the scanned frequencies were used for detection. The

<sup>a)</sup>Electronic mail: jussi.toppari@ju.fi.

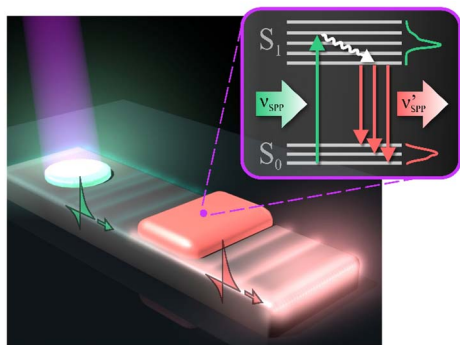


FIG. 1. (Color online) Schematics of the frequency conversion. SPPs are launched by the SPP source (cyan circle) and propagate along the waveguide to the conversion area (red square) with the converter molecules embedded. SPPs are represented in the image as light with corresponding color and by an electric field distribution drawn at the edges of the silvery waveguide. The inset shows a schematic energy diagram of excitation of a converter molecule by SPPs in the conversion area and the coupling back to SPPs. At the end of the waveguide, SPPs are scattered to far field.

image size was  $800 \times 800$  pixels corresponding to an area of  $42 \times 42 \mu\text{m}^2$ . The first scanner controlled the 405 nm laser to locally excite the SPP source, while the second scanner was used to collect emission from the whole sample, resulting in a confocal image as the one shown in Fig. 2(b). The excitation of the SPP source was done in a spiral-like motion of the laser beam (diameter of  $\sim 0.5 \mu\text{m}$ ) over the whole source region. To analyze signals in the frequency domain, emission spectra were recorded with increased sensitivity from different scattering centers, i.e., the positions indicated in Fig. 2(a) (A to D) while exciting the SPP source. Detection area in each position was a diffraction limited spot, about  $\sim 0.5 \mu\text{m}$ , corresponding to the spot size in Fig. 2(a) or smaller. This allows spatially resolved measurements between the different scattering centers. Note that Fig. 2(b) has been taken with lower signal to noise ratio than Fig. 2(a) and the actual spectral measurements, due to the time limitation enforced by bleaching of C30, and does not clearly resolve all the scattering centers. In further analysis, scattering efficiencies are assumed to be identical at each scattering center, i.e., same proportion of the SPP intensity within the waveguide is scattered to the detector at each center. In addition, scattering of SPPs is essentially independent of wavelength; we measured the SPP spectrum at the position D and found it to closely resemble a pure spectrum of C30. The spectra were recorded with the same instrument by scanning the spectral region in 8 nm steps of 30 nm bandpass for R6G and in 4 nm steps of 10 nm bandpass for SR101.

As observed in Fig. 2(b), the signal from the region of C30 (SPP source) is saturated due to direct excitation of this region, while a clear signal is observed in different regions of the waveguide arms. There is no plasmonic channel connected to the lower R6G region, which is manifested by significantly weaker signal caused by far field excitation of R6G by the C30 emission directly through a small solid angle or via scattering in the setup. It is also seen that the SPPs are efficiently scattered from the edges of the waveguides, as well as from the edges of the SU-8 regions due to the change in the refractive index  $n$  ( $n_{\text{SU8}} \approx 1.6$ ). In addition, significantly lower signal from the center of the conversion area compared to its edges is consistent with the coupling of the converter molecules being stronger to SPPs (which then scat-

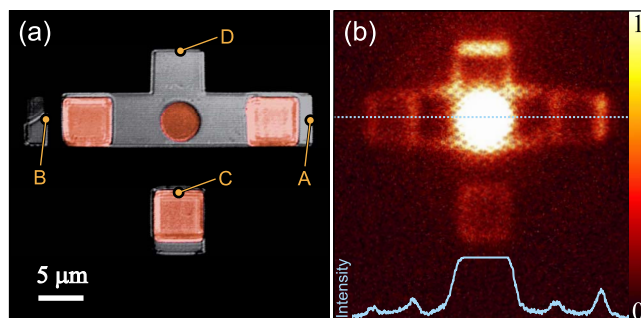


FIG. 2. (Color online) Confocal microscope images of a sample. (a) An image taken by scanning the sample with the excitation light (488 nm) and simultaneously collecting data in two channels. First channel: the gray-blue color corresponds to the reflection image showing the metallic waveguide. Second channel overlaid with the first one: the red color corresponds to a collection band that includes emission from R6G (the red squares) and partly from the C30 (the red circle). The letters correspond to the positions from where the spectra are recorded during the conversion experiment. (b) A plasmon image of the same sample taken with a dual scanner setup where the C30 area in the middle is excited with 405 nm, and emission with a bandpass of 500–600 nm is collected with a second independent scanner. The intensity profile along the blue dotted line is shown below the image.

ter from the edges) than to far field light. Relative intensities at near and far edges of the conversion regions are affected, e.g., by the backscattering of SPPs from the end of the waveguide and thus by the extension of the waveguide after the conversion region in the right hand arm. However, this does not affect the analysis of the frequency conversion efficiency as backscattering is assumed to be the same for the wavelengths considered.

The spectra recorded from positions A and B while exciting C30 are shown in Fig. 3(a), together with reference emission spectra of C30 and R6G (obtained by measuring direct far field emission from similar thin films on silver). The spectra shown are averaged from 2–5 measurements. The spectrum of A clearly shows a combination of C30 and R6G emissions. However, even though B is disconnected from the waveguide, there is a clear contribution of R6G in the spectrum recorded at B, which indicates that the R6G

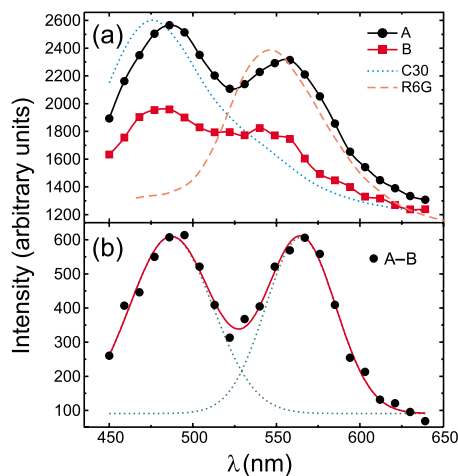


FIG. 3. (Color online) (a) Spectra recorded from the positions shown in Fig. 2(a): A (black circles) and B (red squares). Cyan dotted and red dashed line are the emissions of pure C30 and R6G, respectively. (b) Spectrum of A (black circles) after the subtraction of the spectrum of B, the far field contribution. Red line is a fit to the data as a sum of two Gaussian peaks (green dotted lines) corresponding to the emissions of C30 (480 nm) and R6G (530 nm).

excited by SPPs has also far field emission to B. This emission consists of direct far field emission of the converter molecule and also of scattering of the converted SPPs from the end of the conversion region. Both of these contributions are scattered to the detector by the silver edge at position B. Due to the symmetry of the sample, the same far field contribution can be assumed to be present also in position A. One can thus obtain the pure plasmonic spectrum of A by subtracting the intensity at B from the intensity at A. Note that the spectrum of B contains also converted SPPs that are scattered from the end of the waveguide; therefore, the subtraction gives a minimum estimate of SPP intensity at A. The spectrum of A after the subtraction is shown in Fig. 3(b). In order to obtain the contributions of C30 and R6G in the emission, two Gaussian peaks were fitted to the spectrum in Fig. 3(b) and integrated separately corresponding to C30 and R6G intensities. This yielded 45%/55% distribution between R6G and C30, respectively. Thus the total SPP conversion efficiency of  $\sim 45\%$  was obtained, which is comparable to the efficiencies obtained when using nanoparticle-localized surface plasmons to enhance conversion of far field light.<sup>14</sup>

Scattering from the SU-8 edges due to a nonoptimized geometry is manifested as a high total loss of the plasmonic power. Since position D is as far from the C30 region as the closest edge of the converter area, we can obtain the *input SPP intensity* arriving at the conversion region by measuring the total intensity at D and subtracting from it the far field contribution measured from position C (without R6G). This gives the SPP output, i.e., the intensity at position A, to be 4% and 4.5% of the total input SPP intensity arriving at the conversion region for R6G and C30, respectively. This loss can be explained by analyzing spectra (not shown here) measured from the edges of the SU-8 regions, yielding losses of 25% and 60% by scattering in the edge closer to C30 and far from C30, respectively. In addition, the SPP intensity has an exponential decay with a characteristic propagation length of  $\sim 8 \mu\text{m}$  for this type of waveguide structure,<sup>13</sup> causing about 75% loss in propagation from the source to position A. Together these sources of loss add up to the total loss of over 90% even if assuming directional emission of SPPs from the converter molecules. We have measured tens of samples which all exhibited conversion.

We also measured samples utilizing QDs as the SPP source.<sup>15</sup> QDs overcome the disadvantage of bleaching inherent to dye molecules. The bleaching time of QDs was observed to be over an order of magnitude longer than that of C30. The QDs [Invitrogen, Qdot@ 565 ITK™amino] have an emission maximum at 550 nm if situated near a metal surface<sup>11</sup> (see Fig. 4), and to match this we used SR101, which has an absorption at this wavelength, as a converter molecule (emission maximum at 600 nm). Similar analysis as above yielded 15% conversion. The lower conversion efficiency is due to the smaller overlap between the QD emission and the SR101 absorption. Total SPP losses were similar.

In summary, we have shown that a frequency converter for propagating SPPs can be realized by organic dye molecules (RG6 and SR101). The typical conversion efficiency was around 45%. For device development, the design of the waveguide should be optimized to reduce the losses, which

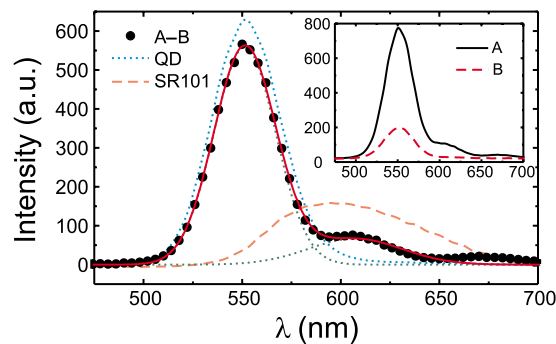


FIG. 4. (Color online) SPP spectrum of A (black circles), i.e., the spectrum of B subtracted from the spectrum of A. The red line is a fit to the data as a sum of two Gaussian peaks (green dotted lines) corresponding to the emissions of QD (565 nm) and SR101 (600 nm). Cyan dotted and red dashed line are the emissions of pure QD and SR101, respectively. Inset shows the spectra recorded from A (black solid) and B (red dashed).

at present are about 90%. We showed that efficient launching of SPPs can be also obtained by QDs, which do not bleach as easily as molecules. QDs could also be used as the converters offering, due to their broad absorption, a multiplexer conversion of a large band into a single frequency. This is complementary to molecules that typically convert one narrow band into another. The possibility of manipulating the emission and absorption of molecules and QDs, e.g., by light or electric fields, offers the prospect of developing active, switchable frequency converters. The use of molecules and QDs also allows a variety of techniques ranging from lithography to self-assembly to be used in fabrication.

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