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Evidence of High-Order Nonlinearities in Supercontinuum White-Light Generation from a Gold Nanofilm

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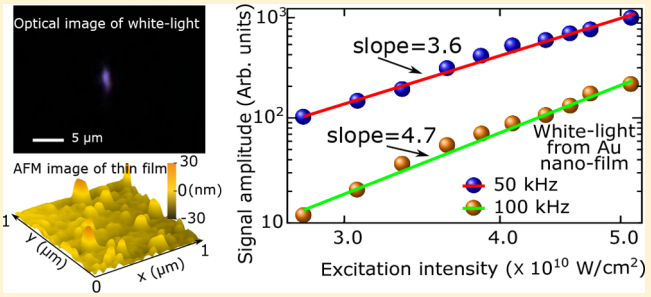
ABSTRACT: White-light supercontinuum generation can be readily observed when gold nanostructures are irradiated with short pulses of light. It is believed that the nanostructures enhance the optical fields, which facilitates the supercontinuum white-light generation from the surrounding environment or the substrate. Here, we investigate the different nonlinear processes that contribute to the generation of the supercontinuum from plasmonic nanostructures themselves using a technique that isolates the different nonlinear contributions. By exciting a gold nanofilm with a pair of frequency shifted optical frequency combs, we demonstrate multiple modulation frequencies in the supercontinuum. Their dependence on the excitation intensity reveals that the supercontinuum originates from different orders of nonlinear light−matter interactions. This contrasts with the supercontinuum generation by a cascaded third-order optical nonlinear response in traditional dielectric-based white-light sources. The while-light emission from the gold nanofilm is efficient even under relatively weak excitation indicating that nonlocal effects in nanostructures may facilitate the supercontinuum generation by adding new pathways in the nonlinear interactions. The results provide experimental basis for the understanding of the collective nonlinear response of free-electrons in the metallic nanostructures and associated nonlinear processes, which are crucial in development of nonlinear metasurfaces and nanophotonic devices.



KEYWORDS: *nonlinear interactions, white-light generation, rough metal films, nonlocal response*

Although gold poorly emits light,[1] its nanostructures are efficient emitters of different kinds of coherent and incoherent radiation when excited with short laser pulses. Two-photon photoluminescence (TPPL)[2−5] is common at low excitation intensity, while high-harmonic[6−9] and supercontinuum (SC) generation[5,10] can be observed at higher intensities. SC generation is also routinely observed when intense pulsed lasers are focused onto any dielectric medium,[11] and it has been suggested that the SC from the gold nanostructures originates due to the emission from the surrounding dielectric medium. The spectral broadening leading to the SC generated from the dielectrics is mainly due to the third-order nonlinear processes such as self-phase modulation (SPM), cross-phase modulation (XPM), and four-wave mixing (FWM). In such a process, the spectral width of the broadened spectrum, $\Delta\omega$, is proportional to the product of the intensity and the interaction length, $\Delta\omega \propto Iz$ (here I is the intensity and z is the interaction length).[11] In a typical dielectric medium, an excitation intensity of 10^{13}−10^{14} W/cm^2 and the interaction length of few millimeters are necessary to observe appreciable spectral broadening. Alternatively, one can substantially increase the interaction length by using guided propagation of pulses in nonlinear optical (NLO) fibers in order to generate broad spectrum at lower excitation intensity.[12−14] The SC from gold nanostructures, on the other hand, is observed at a relatively lower excitation intensity (~10^{10}−10^{11} W/cm^2) as well as very short interaction length (~few tens of nanometers).[10] Although gold nanostructures can locally enhance the electric field, the intensity that is required to generate the SC within the interaction length of few nanometers from the surrounding substrate by SPM, XPM and FWM is about 10^{18} W/cm^2. As metal nanostructures cannot withstand such high intensities, it is unlikely that the SC from the gold nanostructures and the dielectric medium originate from the same nonlinear processes.

The SC generation has not been observed from the bulk gold despite its high intrinsic nonlinearity.[15] Thus, it is reasonable that the optical properties of gold that only manifest in the nanostructures contribute to the nonlinear process. The nonlocal response of free electrons to the incident light fields in metals is one of such properties.[16] Generally, light-matter interactions in dielectric materials are described by the local-response approximation (LRA) in which the electric displace-

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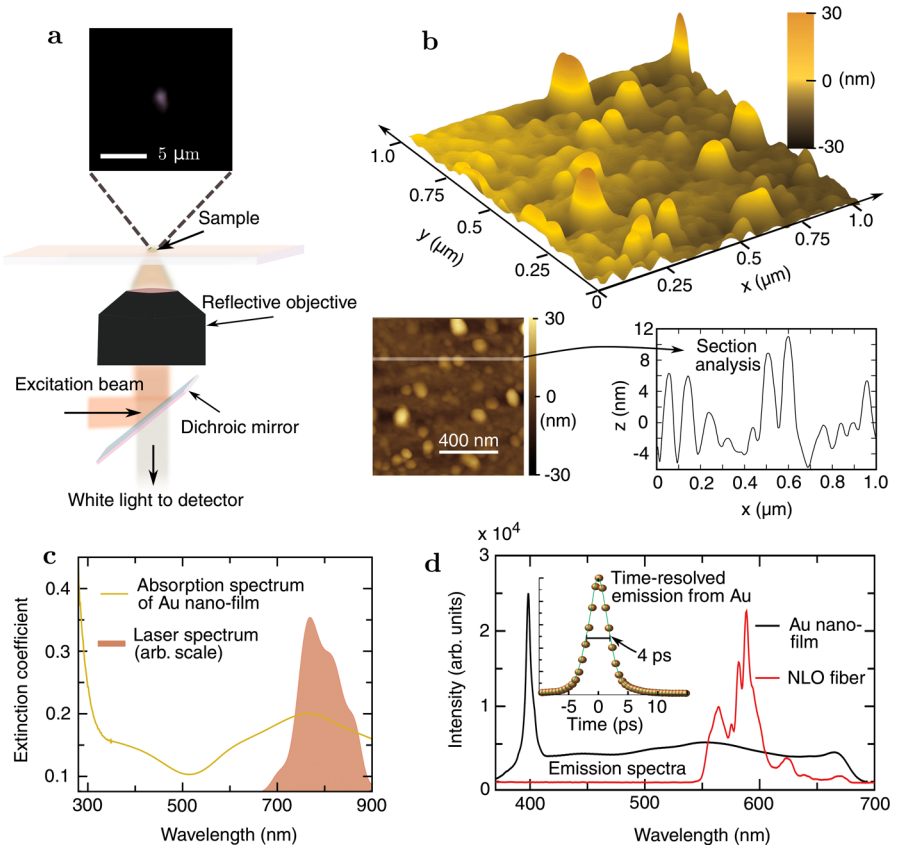

Figure 1. (a) Schematic of the setup used to excite and collect emission from the gold nanofilms and an image of supercontinuum emission from the film. (b) Atomic force microscopy (AFM) image of the film; average surface roughness is about 5 nm. (c) Absorption spectrum of the film and the spectrum of the excitation laser. (d) Spectra of the supercontinuum from the gold nanofilm and the nonlinear optical fiber. Inset in (d) shows the time-trace of the emission recorded by a streak camera. The width of the trace is same as the response time of the detection system (4 ps), which indicates that the lifetime of the emission is significantly shorter than 4 ps.

ment field $\mathbf{D}(\mathbf{r},\omega)$ induced at a point $\mathbf{r}$ by an incident light field of frequency ω is proportional to the locally present field $\mathbf{E}(\mathbf{r},\omega)$. However, the free carriers in conducting media can mediate the response over finite distances, which may not be sufficiently described by LRA.[17−20] In such cases, the displacement field at a point is a cumulative response to the electric field present in the surrounding region (nonlocal response), which is given by

$$\mathbf{D}(\mathbf{r}, \omega) = \varepsilon_0 \int \varepsilon(\mathbf{r}, \mathbf{r}'; \omega)\mathbf{E}(\mathbf{r}', \omega)\mathrm{d}\mathbf{r}' \quad (1)$$

where ε_0 and ε are the dielectric constants of the free space and the medium, respectively. The nonlocal response leads to the excitation of longitudinal plasmon modes that provide additional pathways for light-matter interactions. The longitudinal modes in the bulk, however, do not couple to the external light field. The large surface area of nanostructures, on the other hand, facilitates the coupling of the longitudinal waves in the material to transverse electric field of free space radiation.[17−19,21] Consequently, the effects of the nonlocal response have been observed in various nanosystems[21] but not in the bulk materials, and different theoretical models have been used to explain them.[18,19,21,22] A hydrodynamic model, in which the free electrons are treated as a charged fluid, coupled with Maxwell's equations has often been used to describe the response of the free electrons in metal particles to the light field.[16] Although the nonlocal response is inherently nonlinear,[17,23] most of the previous studies have used linearized hydrodynamic model to investigate the effects of nonlocal response on the linear spectroscopic signals.[18,19,21,24] Few studies have used nonlinear hydrodynamic model to simulate the nonlinear response from metal nanoparticles.[20,25] In this paper, we experimentally study this possibility by separating different nonlinear contributions to the white-light generation and studying their properties. We show that the while-light generated from a rough gold film has broader spectrum under lower excitation intensities than in nonlinear fibers. The increased contribution of higher-order nolinearities in such a system may be facilitated by nonlocal response of free-electron gas.

RESULTS AND DISCUSSION

In the experiments, we have used a microscope setup (Figure 1a) to measure the SC from a gold film with a nanoscale roughness. The average surface roughness of the film measured by an atomic force microscopy (AFM) is about 5 nm (Figure 1b). The extinction coefficient of the sample and the spectrum of excitation laser are shown in Figure 1c. The spectrum of the SC generated from the gold nanofilm (Figure 1d) spans whole of the visible spectrum such that the second-harmonic signal at 400 nm overlaps with the SC when the spectrum of the excitation laser is centered at 800 nm. For comparison, we have also measured spectral broadening in a NLO fiber, where cascaded third-order nonlinear interactions are dominant. The length of the fiber is about 12 cm and the diameter of the core is 1.6 μm. The SC from the fiber has narrower spectral width

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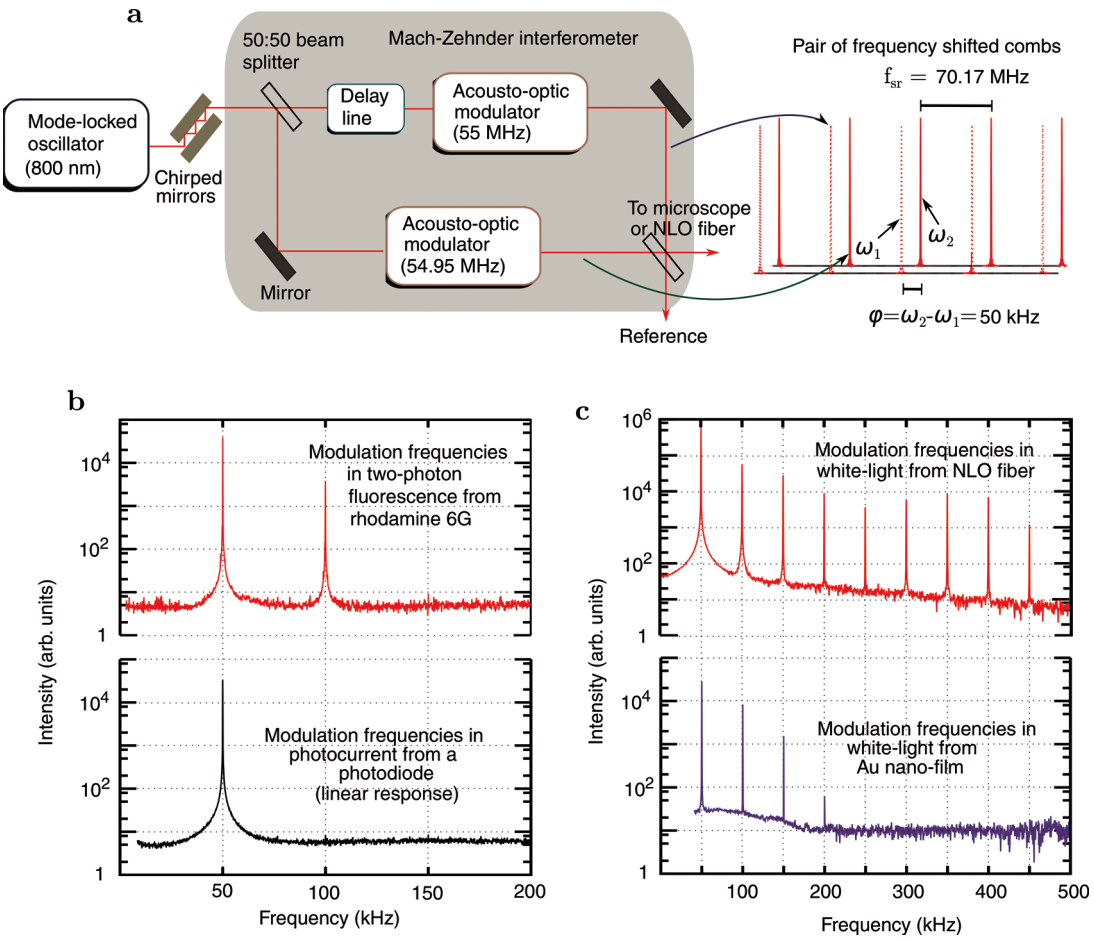

Figure 2. (a) Schematic of the Mach−Zehnder interferometer used to generate a pair of frequency combs. (b) The tooth spacing (free spectral range) of both the combs is identical but their relative offset frequency differ by 50 kHz. (b, c) The Fourier transforms of different linear and nonlinear signals excited by the pair of frequency combs. In (b), lower panel is the photocurrent from a Si photodiode (linear response) and upper panel is the two-photon fluorescence from Rhodamine 6G. In (c), lower panel is the SC generated from the gold nanofilm (excitation intensity is about 2×10^{11} W/cm^2) and upper panel is the SC generated from the NLO fiber (excitation intensity is about 10^{12} W/cm^2).

with a sharp cutoff at the visible wavelengths even at the excitation intensity of 10^{12} W/cm^2.

Previous measurements done by Mühlschlegel et al.[5] and Biagioni et al.[26] show that the SC from gold nanoantennas scale with the fourth power of the excitation intensity. However, such dependence alone does not ascertain the order of nonlinear interaction if the signal arises from different nonlinear processes. As the nonlinear response based on the nonlocal interactions suggests that different orders of nonlinearity contribute to the SC, we have used a novel technique of phase-sensitive detection (PSD)[27] to disentangle the nonlinear processes that contribute to the SC. The PSD scheme uses interferometry of a pair of frequency combs that originate from the same mode-locked oscillator (Figure 2a). In our measurements, both combs have a tooth spacing of 70.17 MHz but the frequencies of the corresponding teeth in the combs, ω_1 and ω_2, differ by ϕ = 50 kHz (i.e., the offset frequencies differ by 50 kHz). It is well-known that the signals generated by the linear interaction of such two combs in a sample, such as, for example, photocurrent, are modulated at a frequency ϕ (lower panel in Figure 2b), while the contributions at higher multiples of ϕ are due to the signals that arise from the nonlinear interactions.[27,28]

We first compare the signal observed in a typical TPPL from a dye and the SC from the gold nanofilm. The TPPL from rhodamine 6G (Figure 2b (upper panel)) gives contributions at ϕ and 2ϕ modulation frequencies. The contributions at these two frequencies is a general feature of the signals arising from a two-photon absorption[27] process. Here, it is also important to note that artifacts at higher modulation frequencies can arise if the lifetime of the fluorescence is longer than the repetition rate of the laser.[28] As the fluorescence lifetime in rhodamine 6G is about 4 ns, which is substantially shorter than the repetition time of the excitation pulses (about 14 ns), it is free from such artifacts. Similarly, the emission lifetime from gold nanofilm has been reported to be shorter than few picoseconds. Our measurement of the emission lifetime using a streak camera (the inset in Figure 1d) is limited by the response time of the detection system (4 ps), which suggests that the lifetime is substantially shorter. Thus, two-photon induced emission under the experimental condition is expected to show modulations at the two frequencies. However, our measurements show modulations up to 4ϕ in the SC from the gold nanofilm. Therefore, the SC from the nanofilm is not only the TPPL emission. The highest modulation of 4ϕ suggests that the high order interactions, possibly with different orders of nonlinearity, contribute to the SC generation.

Next, we compare the modulations observed in the SC from a NLO fiber and the gold nanofilm. As shown in Figure 2c, modulations at all the harmonics of ϕ are present in the SC from the NLO fiber. However, these modulations are not due

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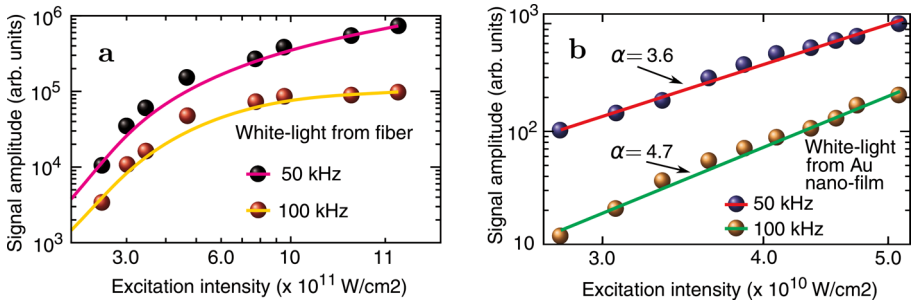

Figure 3. Dependence of the signal amplitudes at 50 and 100 kHz on excitation intensity, I, for the white-light supercontinuum generated in a nonlinear fiber (a) and the gold nanofilm (b). The amplitudes in (a) show saturation at high excitation intensity while the amplitudes in (b) show a power law increase $\propto I^{\alpha}$ at all the intensities. Different values of α indicate that the signals arise from nonlinear processes of different orders.

to high-order nonlinear interactions but from a cascaded FWM process,[29] which is a third-order interaction.[12] A FWM of two frequencies ω_1 and ω_2 produces new comb frequencies at $\omega_1 \pm \phi$ and $\omega_2 \pm \phi$. The long interaction length in the fiber facilitates the repeated FWM with the new frequencies that eventually leads to the generation of comb lines at a regular spacing of ϕ. In order to distinguish if the modulations in the SC from a gold nanofilm are related to the cascaded FWM or the higher-order nonlinear interactions, we compare the relative amplitudes of the signals at the different modulation frequencies. The amplitudes at the higher modulation frequencies decrease rapidly in the SC from gold nanofilm, which is characteristic of high-order nonlinear interaction. Such clear trend is not observed in the SC from the fiber. In fact, the signals at 6, 7, and 8ϕ are stronger than the signal at 5ϕ.

The intensity dependence of the SC also helps us to disentangle the underlying processes. Unlike the previous measurements, where only average power of the SC were measured,[5,26] we have measured the signals at the different modulation frequencies. Figure 3 shows the signal amplitude as a function of excitation intensity at the modulation frequencies ϕ and 2ϕ in the SC from the NLO fiber (a) and the gold nanofilm (b). For the SC from the fiber, we observe a clear saturation of the signals at the lower modulation frequencies (Figure 3a) with the appearance of the signals at higher modulation frequencies (Figure 2c, upper panel). The signals at the higher modulation frequencies is due to the transfer of amplitude from the lower modulation frequencies via cascaded FWM processes. We note that appreciable spectral broadening is observed only at the excitation intensities above 10^{12} W/cm^2, which is an order of magnitude higher than the intensity at which the SC generation is observed in the gold nanofilm. In contrast to the modulated signals from the NLO fiber, the signals from the gold nanofilm increase with higher powers of the excitation intensity, which is characteristic of the contributions from noncascaded nonlinear processes.

It is important to note that the slopes of the intensity dependences of the signals at ϕ and 2ϕ frequencies are 3.6 $\pm$ 0.1 and 4.7 $\pm$ 0.2, respectively (Figure 3b): if the amplitudes at ϕ and 2ϕ frequencies would have the same slope, both the signals would originate from the same nonlinear process.[27] This further ascertains that the SC from the gold nanofilms do not arise from a third-order light−matter interaction but from higher-order nonlinearities.[27] Conventionally, the higher-order nonlinearities require higher excitation intensities to become comparable with lower-order nonlinear contributions; however, if a nonlocal nonlinear response from free-electrons in nanoscale plamonic structures is present, higher-order nonlinearity may become important even at lower excitation intensities.[20] Thus, the contribution from higher-order nonlinearities increases faster in the system with a nonlocal response than with the local one, leading to the increased total radiated nonlinear generation. This effect may be a significant factor in the observed efficient SC generation from nanoscale plasmonic films.

Recent studies demonstrated a nonlocal optical response from the gold films of a 5 nm nominal thickness which consist of nearly percolating nanoislands of gold with a subnanometer interisland separations.[30] Interestingly, white-light generation has been found to be the most efficient in such films. Theoretical models suggest that the nonlocal response dampen the local transverse electromagnetic field and facilitates excitation of the longitudinal modes.[22] Accordingly, one would expect the nonlinear optical response from the bulk which is associated with the transverse field components to be suppressed by the nonlocal effects. Nevertheless, the longitudinal modes excited due to the nonlocal effects open up new pathways of efficient nonlinear interactions, which may contribute to the observed high-order nonlinearity and the white-light generation in the nanofilms.

CONCLUSION

We have investigated the SC generation from the gold films with nanoscale roughness and showed that the nonlinear emission is not due to the cascaded third-order processes in the substrate but due to higher-order nonlinear processes in the plasmonic film itself. The observed SC emission spectrum at moderate excitation intensities are broader than the SC spectrum of the fiber at much higher excitation intensity. The spectrum of the SC and its intensity scaling indicate that nonlinearity associated with the nonlocal response of the free-electrons in the nanofilms may contribute to the nonlinear response. The observed effects are important for the description of light-matter interactions with nanoscale plasmonic structures and should be considered in the design of nonlinear nanophotonic devices.

MATERIALS AND METHODS

Sample Preparation and Characterization. Ultrathin gold film (5 nm nominal thickness) was deposited on a clean glass slide (Thermo Scientific Microscope Slides) by using magnetron sputtering (AJA Orion 5 sputtering system). At a 5 nm nominal thickness, isolated, 3D metal islands formed on the substrate surface,[31] which was confirmed by an AFM image and an optical transmittance spectrum. AFM (Digital Instrument, Dimension 3100) was employed to observe surface morphol-

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ogy of the thin gold film at a scan rate of 0.5 Hz. The transmittance spectrum of the thin gold film was taken by using Agilent 845x UV−visible spectrophotometer. A surface plasmon excitation was observed at the wavelength of about 800 nm. A Ti:sapphire oscillator (Tsunami, Spectra Physics) was used as the excitation light source for measuring the spectrum and lifetime of the SC emission. The oscillator produced pulses with a duration of about 35 fs at a repetition rate of 80 MHz. The center wavelength of the femtosecond pulse train was at 800 nm. The spectrum of the SC white-light, which was generated by exciting the nanofilm with the femtosecond pulses, was measured by using a picosecond streak camera (C6860, Hamamatsu). The streak camera was coupled to a Chromex spectrograph and triggered by the Ti:sapphire oscillator. A short-pass wavelength filter at 675 nm was used in front of the spectrograph to cut off the scattering from the excitation pulses. The measurement of the lifetime of the emission was limited by the response time (4 ps) of the detection system in the streak camera.

Measurements of the Different Nonlinear Signals Using a Dual Frequency Comb Interferometry. The schematic of the Mach−Zehnder interferometer, which was used to generate a pair of frequency combs, is shown in Figure 2a. A Ti:sapphire oscillator (Synergy, Femtolasers) was used as the light source. The repetition rate of the oscillator was 70.1 MHz and the pulse duration was about 15 fs. A pair of chirp mirrors were used to compensate the group-velocity dispersion induced by the beam splitters and the AOMs. The beam from the oscillator was split into two identical replicas by a 50:50 beam splitter. The carrier offset frequencies (COF) of the two beams were shifted using AOMs in the arms of the Mach−Zehnder interferometer. The COF of one of the beams was shifted by 55 MHz, while that of the other was shifted by 54.95 MHz. The two beams were combined in a second 50:50 beam splitter. The temporal overlap between the two beams was optimized using a piezo driven delay stage. One of the outputs of the interferometer was directed to an inverted microscope (Nikon Ti−S). A reflective objective (36×/0.5 NZ, Edmund Optics) was used to focus the beam onto the gold nanofilm sample. The SC white-light emission from the sample was collected using the same microscope objective. A dichroic mirror (FF670-SDi01-25x36, Semrock), was used to separate the emission from the excitation beam. Another OD 4 short-pass filter with cutoff at 625 nm was used to further suppress the scattered excitation beam. An APD (LCSA3000-01, Laser Components) was used to detect the emission. The electronic signal from the APD was digitized at the rate of 20×10^6 samples per second by using a 14 bit digitizer (ATS9440, AlazarTech). The digitized signals were analyzed by using Fast Fourier Transforms or a generalized lock-in amplifier.[32] The second output of the Mach−Zehnder interferometer was directed to a SC generation kit (SCKB, Thorlabs). The white-light from the SC generation kit was detected by an amplified photodiode (PD36A, Thorlabs). The signal from the photodiode was digitized and analyzed similarly to the signal from the APD.

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Notes

The authors declare no competing financial interest.

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