High-Efficiency Second Harmonic Generation from a Single Hybrid ZnO Nanowire/Au Plasmonic Nano-Oligomer

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1- Fabrication of plasmonic Au pentamers

Arrays of Au pentamers were fabricated by electron beam lithography on a fused silica substrate. First the substrate was coated with a positive resist (PMMA) and was baked at ~180 °C for 120 seconds. Then antennas were defined by an electron beam exposure, followed by development procedure. Subsequently, a 3 nm thick Cr film was deposited by e-beam evaporation on the substrate (to increase the Au adhesion) followed by 60 nm Au film. Lift-off and Oxygen plasma were the last steps of fabrication.

Figure S1. An illustration of fabrication steps for the Au pentamer array.
2- ZnO nanowires growth

ZnO NWs were fabricated via VTD (vapor transport and deposition) over commercial carbon fiber fabric (composed by 5 μm diameter carbon fibers). The growth system includes a continuously pumped quartz tube within a tubular furnace with mass flow controlled Ar and O\textsubscript{2} flow rates. A flow rate ratio of 6\% (O\textsubscript{2}/Ar) at a working pressure of ~1 Torr was chosen. A crucible with the ZnO precursor powder (ZnO+C, 1:1 in weight) was positioned at the furnace center at 1000 °C, while the substrate was put 9 cm downstream the quartz tube, where the temperature was ~900 °C due to a natural temperature gradient along the furnace axis. The deposition time was set to 1 hour. Figure S2(a) shows a SEM image of the grown sample, presenting several carbon fibers fully covered with ZnO NWs. Figure S2(b) exhibits an expanded view where size and shape of the NWs can be appreciated.

![Figure S2: (a) SEM image of the ZnO NWs sample. Scale bar, 20 μm. (b) Close view of the surface of a carbon fiber with ZnO NWs. Scale bar, 500 nm.](image)
3- Construction of hybrid ZnO nanowire/Au plasmonic nanoantenna

ZnO NWs were transferred from the carbon fibers to the plasmonic substrate by a dry printing process. As it can be seen in Figure S3, just a minor portion of the transferred NWs result conveniently located in the sample. Reason of this, is that the gaps between the Au disks represent only about 0.1% of the total surface area in a substrate patterned with 1μm pitch. This is one of the motives why we chose four-gaps pentamer-like antennas instead of simpler single-gap dimer-like ones, which would generate hot-spots in a surface area a factor of 4 lower for the same pitch. 1-2% is the best we could achieve in proportion of pentamers turned into single hybrid nanoantennas over total number of pentamers. One way to improve effectiveness would be reducing the pitch, but this would cause coupling between neighboring nanoantennas. The same would occur for the NWs if repeating the printing process to increase number of NWs in the sample.

Figure S3: SEM image of ZnO NWs over the plasmonic substrate. Scale bar, 500 nm. Only one of the three NWs in the image is crossing a pentamer’s gap.
4- Optical measurements details

Extinction measurements of the pentamer arrays were obtained by Fourier transform infrared spectroscopy (FTIR, Bruker Hyperion 2000) at normal incidence with linear polarization. PL characterization of the ZnO NWs was made with a 15 mW He-Cd laser from Kimmon Koha Co. at 325 nm as the excitation source (2 mm diameter beam spot), and the emission was collected in a back-scattering geometry with a AvaSpec-ULS3648 fiber-optic spectrometer. SHG intensity measurements and SHG images were obtained with a home-made confocal microscope (sketched in Figure 2a). For the excitation a pulsed Ti:Sa laser from KM Labs (780-810 nm, 50 fs pulse width, 90 MHz repetition rate) was focused onto the sample with a 40X (NA=0.6) air objective from Olympus. The SHG emission was collected in a confocal back-scattering configuration and detected with a cooled photomultiplier tube from Hamamatsu in counting mode. The sample was fixed to a XYZ piezo-scanner stage from Physik Instrumente to perform the scanning. SHG spectrum measurements from the nanostructures were made in a home-made wide-field microscope coupled to a Raman spectrometer (U1000 Jobin-Yvon) and a cooled CCD camera from Horiba.
5- SHG from bare nanoantennas

SHG intensity from bare nanoantennas was found to vary typically no more than \( \sim 20\% \) between different nanostructures. This variability can be appreciated at Figure S4(a), which shows the \( I_{\text{SHG}} \) profile of a line of 5 pentamers excited at \( \lambda_{\text{exc.}} = 780 \) nm. Figure S4(b) compares \( I_{\text{SHG}} \) vs. \( \lambda_{\text{exc.}} \) between the hybrid nanostructure and a single bare nanoantenna. For the last, \( I_{\text{SHG}} \) is about 1 order of magnitude lower.

Figure S4: (a) \( I_{\text{SHG}} \) measured profile along the x-axis of 5 pentamers in line excited at \( \lambda_{\text{exc.}} = 780 \) nm. (b) \( I_{\text{SHG}} \) vs. \( \lambda_{\text{exc.}} \) for the hybrid nanoantenna and a single pentamer.
6- Hybrid nanoantenna off-resonance

When the experiment is performed for a hybrid nanostructure with the plasmonic resonance far from the excitation wavelength, no SHG enhancement effect is noticed. Figure S5(a) shows a SEM image of an array of 3x2 pentamers with a ZnO NW crossing at least one gap of one of the nanoantennas. For these pentamers the plasmonic resonance occurs at \( \sim 930 \) nm (Figure S5(c)). Figure S5(b) exhibits a SHG image at \( \lambda_{\text{exc.}} = 810 \) nm, where no appreciable difference is found between the NW excited at or outside the nanoantenna region. The same result was found exciting at lower wavelengths.

Figure S5: (a) SEM image of a ZnO NW over a plasmonic substrate. Scale bar, 500 nm. (b) SHG image of (a) at \( \lambda_{\text{exc.}} = 810 \) nm. (c) Measured extinction spectrum of the pentamers prior ZnO NWs deposition.