Surface plasmon resonance spectroscopy of single bowtie nano-antennas using a differential reflectivity method

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We report on the structural and optical properties of individual bowtie nanoantennas both on glass and semiconducting GaAs substrates. The antennas on glass (GaAs) are shown to be of excellent quality and high uniformity reflected by narrow size distributions with standard deviations for the triangle and gap size of \( \sigma_{\text{glass}} = 4.5 \text{ nm} \) \( \sigma_{\text{GaAs}} = 2.6 \text{ nm} \) and \( \sigma_{\text{glass}} = 5.4 \text{ nm} \) \( \sigma_{\text{GaAs}} = 3.8 \text{ nm} \), respectively. The corresponding optical properties of individual nanoantennas studied by differential reflection spectroscopy show a strong reduction of the localised surface plasmon polariton resonance linewidth from 0.21 eV to 0.07 eV upon reducing the antenna size from 150 nm to 100 nm. This is attributed to the absence of inhomogeneous broadening as compared to optical measurements on nanoantenna ensembles. The inter-particle coupling of an individual bowtie nanoantenna, which gives rise to strongly localised and enhanced electromagnetic hotspots, is demonstrated using polarization-resolved spectroscopy, yielding a large degree of linear polarization of \( \rho_{\text{max}} \sim 80\% \). The combination of highly reproducible nanofabrication and fast, non-destructive and non-contaminating optical spectroscopy paves the route towards future semiconductor-based nano-plasmonic circuits, consisting of multiple photonic and plasmonic entities.

Single metal nanoparticles1, nanoparticle dimers2 or even nanoparticle arrays3 are well known to concentrate visible4, infrared5 and microwave6 radiation from the far-field into sub-wavelength sized optical volumes whilst simultaneously giving rise to strong electric field enhancements7,8 on the order of \( 10^3 \) – \( 10^5 \). In particular optical antennas9 such as bowtie nanoantennas have been shown to provide besides extraordinarily high field enhancements10, also directionality11, broadband spectral responses12, local electrical control13 with potential for tunability14, highly efficient electro-optical driving15 and full polarization control16. Amongst others, such systems found already applications in surface enhanced Raman spectroscopy17, ultra-high resolution lithography18 and microscopy19, bio-chemical sensing20,21, spontaneous emission control22 and enhancement23,24, non-linear optics25,26 and solar energy conversion27.

Chemical synthesis28 of plasmonic nanostructures is well established and widely-used since sophisticated and expensive equipment is not required to produce large amounts of plasmonic nanoparticles. However, nano-lithography techniques offer much higher flexibility in controlling and deterministically designing the optical properties of plasmonic nanostructures. For example, it is possible to tailor the localised surface plasmon polariton resonance via precise adjustment of size29,30 and shape14, as well as the polarization of the scattered photons via the antenna geometry16. Moreover, the exact control of the particle location and density during the lithography process enables to switch on radiative coupling in arrays of nanoparticles12 and, thus, give rise to multipolar surface plasmon modes33 and collective surface lattice resonances34. This proves crucial to design novel properties such as magnetic polarizability35, negative-refractive indices36 or phase-gradients37 in metasurfaces38.

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Many spectroscopy techniques for studying single plasmonic nanostructures have been established in recent years\(^{39}\). Examples include scanning near-field optical microscopy\(^{40}\), attenuated total internal reflection\(^3\), extinction or transmission experiments\(^4\) and dark field spectroscopy\(^{41}\). However, the majority of those methods either demand expensive equipment, require specially designed samples or contaminate their surface. Therefore, a reliable, fast, non-destructive and cheap measurements method with high spatial resolution would be highly attractive for determining the optical properties of the individual plasmonic nanostructures on a future semiconductor-based plasmonic nano-circuit\(^{42,44}\).

Here, we present a systematic and comprehensive study of the structural and optical properties of individual, lithographically defined bowtie nanoantennas\(^{12}\) on glass and semiconducting GaAs substrates using differential reflection spectroscopy. Therefore, we fabricated antennas with sizes \(100 \, nm \leq s_0 \leq 150 \, nm\), feed-gaps down to \(5 \, nm\) and tip radii \(r_t = 14 \pm 5 \, nm\) using electron beam lithography\(^{30}\). Scanning electron microscopy yields narrow distributions of triangle size and gap size on glass (GaAs) substrates with standard deviations of \(\sigma_{s}^{\text{GaAs}} = 4.5 \, nm\) and \(\sigma_{g}^{\text{GaAs}} = 5.4 \, nm\), respectively, indicating highly uniform and reproducible nanofabrication. The corresponding optical properties of individual bowtie nanoantennas are investigated using high-spatial resolution, differential reflection spectroscopy, demonstrating the linear (inverse cubic) dependence of the surface plasmon resonance energy \(E_{\text{sp}}\) on the triangles size (gap size)\(^{12,30}\). Comparison between measurements on single and ensembles of bowtie nanoantennas\(^{30}\) show clear indications of inhomogeneous broadening\(^3\), varying between \(0.07 \, eV\) and \(0.21 \, eV\) for \(s_0 = 100 \, nm\) and \(s_0 = 150 \, nm\), respectively. Finally, we study the inter-particle coupling between the two nano-triangles forming the bowtie nanoantenna using polarization-resolved spectroscopy. Those measurements show strongly linearly polarized emission along the main axis of the antenna for the coupled mode with a degree of polarization up to \(\rho_{\text{max}} \approx 80\%\). Our results are contrasted with studies on semiconductor GaAs substrates and all experiments are shown to be in excellent agreement with numerical simulations\(^{44}\).

Results

In Fig. 1(a), we present a selection of scanning electron microscopy images of lithographically defined Au bowtie nanoantennas on a non-conducting glass substrate, consisting of two nominally equilateral nano-triangles, arranged in a tip-to-tip-configuration\(^{11,40}\). The top (bottom) row shows bowtie nanoantennas for constant nominal triangle size \(s_0 = 140 \, nm\) (gap size \(g_0 = 10 \, nm\)) and increasing \(g_0\) from \(5 \, nm\) (100 nm) and \(50 \, nm\) (150 nm) from left to right, respectively. The antenna thickness was kept constant at \(t = 35 \, nm\). The triangles forming the bowtie nanoantenna are of high quality, indicated by their smooth edges and surfaces without observable distortions or fraying. The typical tip radii was found to be \(r_t = 14 \pm 5 \, nm\). The highly reproducible fabrication process is further supported by the histograms plotted in Fig. 1(b), representing the number of individual bowtie nanoantennas as a function of triangle size deviation \(\Delta s = s - s_0\) and gap size deviation \(\Delta g = g - g_0\) in the left and right panel, respectively. Here, \(s\) and \(g\) denote the experimentally determined triangle and gap size, respectively, as defined in the leftmost images in Fig. 1(a). We extracted \(s\) and \(g\) from high resolution scanning electron microscopy measurements for ~300 nominally identical bowtie nanoantennas without any pre-selection, with \(s_0\) and \(g_0\) spanning the range given in Fig. 1(a). Both histograms for \(\Delta s\) and \(\Delta g\) are well described by a Gaussian distribution \(y(x) = \frac{\Lambda}{\sigma_{s}^{\text{GaAs}}} \exp\left(-\frac{(x-\mu)^2}{2 \sigma_{s}^{\text{GaAs}}} \right)\) where \(\mu\) and \(\sigma\) denote the expectation value and the standard deviation, respectively. From the fits of the triangle size and gap size histograms, we obtain narrow distributions indicated by the small values of the corresponding \(\sigma_{s}^{\text{GaAs}} = 4.5 \, nm\) and \(\sigma_{g}^{\text{GaAs}} = 5.4 \, nm\). This means in particular that ~95.4% of the fabricated triangles exhibit deviations in triangle size and gap size of less than \(2\sigma_{s}^{\text{GaAs}} = 9 \, nm\) and \(2\sigma_{g}^{\text{GaAs}} = 10.8 \, nm\) from the nominal values, respectively. We further note that the shift of both triangle and gap size distributions from \(\Delta s = 0\) and \(\Delta g = 0\), reflected by \(\mu_{s}^{\text{GaAs}} = 3.1 \, nm\) and \(\mu_{g}^{\text{GaAs}} = 2.4 \, nm\), can easily be compensated by fine-adjusting the dose during the electron beam lithography. Similar structural investigations for Au bowtie nanoantennas on high-refractive index (\(n_{\text{GaAs}} = 3.54\) at \(T = 297 \, K\) and \(E_{\text{phot}} = 1.3 \, eV\))\(^{45}\), semiconducting GaAs substrates showing even narrower distributions with \(\sigma_{s}^{\text{GaAs}} = 2.6 \, nm\) and \(\sigma_{g}^{\text{GaAs}} = 3.8 \, nm\) are presented in the Supplementary Material, Fig. SM1. We conclude that we established a highly reproducible lithography process for bowtie nanoantennas with a fabrication accuracy of ~10 nm, giving rise to reproducibly fabricated nanoantennas with feature sizes down to 10 nm. We note that bowtie nanoantennas with gap sizes \(g < 10 \, nm\) are not reproduced with 100% yield due to the ~10 nm resolution limit of the used electron beam system. Therefore, sub-10 nm gap sizes can only be obtained based on a statistical approach and imaging is impeded in particular on non-conducting substrates due to charging effects. However, we could clearly distinguish antennas with sub-10 nm gaps from clustered antennas in the optical characterisation and comparison with the corresponding simulations, since clustered antennas give rise to spectrally detuned localized surface plasmon polariton resonance.

To study the optical response of individual bowtie nanoantennas, we used a home-built confocal microscope that facilitates measurements of the broadband (\(\Delta \lambda \sim 400 - 1600 \, nm\)) reflectivity of a diffraction limited laser spot generated by a white-light super-continuum source as schematically shown in Fig. 2(a). The excitation beam is, if not stated otherwise, linearly polarized along the long axis of the bowtie nanoantenna (defined as y-axis in Fig. 1(a)), reflected from a beamsplitter and focused onto the sample via a microscope objective. The reflected light is collected via the same objective, transmitted through the beamsplitter and guided via an optical fibre to a spectrometer. For more details on the setup and the used optical components we refer to the Methods Section. In order to determine the localised surface plasmon polariton resonance of an individual nanoantenna, we performed two subsequent measurements; first, we measured the reflectivity \(R_{\text{nm}}(E)\) from an individual bowtie nanoantenna as a function of energy \(E\) as shown by the red curve in Fig. 2(b). Here, the upper inset depicts a light microscopy image recorded in our setup, which displays the bowtie nanoantennas (\(s_0 = 140 \, nm\), \(g_0 = 10 \, nm\))
arranged in a periodic array with a lattice constant of \( a = 1.5 \mu \text{m} \) and the white light excitation spot focused on one single antenna. In a second step, we recorded a similar reflectivity spectrum \( R_{\text{off}}(E) \) from a location spatially displaced from the bowtie nanoantenna array as shown by the lower inset in Fig. 2(b) for reference. The corresponding spectrum \( R_{\text{off}}(E) \) is plotted in blue. From the measurements of \( R_{\text{on}}(E) \) and \( R_{\text{off}}(E) \) we calculate the differential reflectivity \( \Delta R/R_{\text{off}} \equiv (R_{\text{on}} - R_{\text{off}})/R_{\text{off}} \), which represents a measure for the scattered light from the bowtie nanoantenna\(^{46}\). The \( \Delta R/R_{\text{off}} \)-spectra determined from the reflectivity measurements shown in Fig. 2(b) is presented in panel (c). We observe a peak-like response with a resonance maximum \( \gamma_{\text{res}} \) at the resonance energy \( E_{\text{res}} \), interpreted as the dipolar localised surface plasmon polariton resonance of the investigated bowtie nanoantenna\(^{39}\). Furthermore, we can extract from the differential reflectivity spectrum the full width at half maximum \( \Gamma_{\text{res}} \) and, thus, gain insights into the related plasmon lifetime \( T_{\text{pl}} \) via \( T_{\text{pl}} = 2\hbar/\Gamma_{\text{res}} \), where \( \hbar \) denotes the reduced Planck constant.

In the following, we use our method to systematically study the optical properties of individual bowtie nanoantennas fabricated on both glass and GaAs substrates as a function of \( s_0 \) and \( g_0 \). The experimentally obtained \( \Delta R/R_{\text{off}} \)-spectra for \( g_0 = 10 \text{ nm} \) and triangle sizes \( 100 \text{ nm} < s_0 < 150 \text{ nm} \) in steps of \( \Delta s_0 = 10 \text{ nm} \) are presented in Fig. 3(a) for bowtie nanoantennas on glass. We observe a systematic shift of the localised surface plasmon polariton resonance from \( E_{\text{res}} = 1.39 \text{ eV} \) to higher energies \( E_{\text{res}} = 1.73 \text{ eV} \) with decreasing \( s_0 \), attributed to reduced retardation effects of the exciting electromagnetic field and the depolarization field inside the metal particles\(^{47}\). The blue-shift in \( E_{\text{res}} \) is accompanied by a decreasing resonance maximum \( \gamma_{\text{res}} \) from \( \gamma_{\text{res}} = 1.37 \) to \( \gamma_{\text{res}} = 0.67 \), which is due to a reduction of the geometrical scattering cross-section of the antennas with decreasing \( s_0 \). In Fig. 3(b), we present corresponding finite-difference time-domain simulations\(^{44}\) of the scattering cross-section \( \sigma \) for bowtie nanoantennas on a glass substrate with \( g_0 = 10 \text{ nm} \), \( r_c = 20 \text{ nm} \) and varying triangle size \( 100 \text{ nm} < s_0 < 150 \text{ nm} \). We
find increasing $E_{\text{res}}$ and decreasing $\gamma_{\text{res}}$ with decreasing $s_0$, both in excellent qualitative and quantitative agreement with our experimental results. We compare the measured and simulated data for $E_{\text{res}}$ as a function of $s_0$ and $g_0$ in Fig. 3(c,d), respectively. Blue (black) symbols denote the experimental results for bowtie nanoantennas on a glass (GaAs) substrate, whilst the red symbols represent the simulation results. In general, we observe a comparable linear (cubic) trend for the $s_0$- ($g_0$-) dependence of bowtie nanoantennas on glass and GaAs with shift-rates for the $s_0$-dependence of $-(6.8 \pm 0.3) \text{ meV/nm}$ and $-(6.3 \pm 0.2) \text{ meV/nm}$, respectively. The global red-shift of the GaAs data of $\Delta E \sim 0.3 \text{ eV}$ is due to the increase in refractive index of $\Delta n \sim 2.0$ as compared to glass$^{30}$. The cubic $\propto g_0^{-3}$ behaviour observed in the gap size dependence in Fig. 3(d) is due to near-field interaction, describing the coupling of the surface plasmons in the two adjacent triangles by a coupling of effective point dipoles$^{48}$. Simulations of the spatial electromagnetic field distribution for similar bowtie nanoantennas are presented in ref. 30. Additional spectra and the corresponding simulated scattering cross-sections for the $g_0$-dependence on glass and the $s_0$- and $g_0$-dependence on GaAs, respectively, are presented in Fig. SM2. As a consequence, we experimentally studied localised surface plasmon polariton resonances for individual bowtie nanoantennas using differential reflection spectroscopy and obtained excellent agreement with numerical simulations of the scattering.
cross-sections. This combined experimental-simulation approach enables us to reproducibly design and
deterministically control the localised surface plasmon polariton resonance of individual nanoantennas.

As demonstrated in the previous section, the localised surface plasmon polariton resonances of bowtie
nanoantennas depend strongly on the triangle size $s_0$ and gap size $g_0$. Even though our fabrication process was shown to
be highly reproducible, slight variations in $s_0$ and/or $g_0$ will still result in non-negligible variations of the localised
surface plasmon polariton resonances. Therefore, measurements on ensembles of bowtie nanoantennas as inves-
tigates in ref. 30 are expected to show enlarged resonance linewidths $\Gamma_{\text{res}}$ due to size- and shape-induced inhomogene-
ous broadening. To test this hypothesis, we compare in Fig. 4(a) two typical differential reflectivity spectra

Figure 3. (a) Differential reflectivity $\Delta R/R_0$ and (b) numerically simulated scattering cross-section $\sigma$ as a
function of energy $E$ for triangle sizes $100 \text{ nm} < s_0 < 150 \text{ nm}$ and $g_0 = 10 \text{ nm}$. (c) Localised surface plasmon
polariton resonance energy $E_{\text{res}}$ as a function of triangle size $s_0$ for $g_0 = 10 \text{ nm}$ on a glass and a GaAs substrate in
blue and black, respectively. (d) Localised surface plasmon polariton resonance energy $E_{\text{res}}$ as a function of gap size $g_0$ for $s_0 = 140 \text{ nm}$ on a glass and a GaAs substrate in blue and black, respectively. Red symbols and curves in
(c,d) represent simulation results.

Figure 4. (a) Differential reflectivity $\Delta R/R_0$ as a function of energy $E$ and gap sizes $g = 10 \pm 3 \text{ nm}$ for a bowtie
ensemble and a single bowtie nanoantenna on a glass substrate plotted in black and blue, respectively. Insets:
(Left) Light microscopy images of the bowtie field under illumination with a halogen lamp and the white light
super-continuum source in black and blue, respectively. (Right) Same data shown on a normalized differential
reflectivity scale. (b) Full width at half maximum $\Gamma_{\text{res}}$ as a function of triangle size $s$ for bowtie ensembles and
single bowtie nanoantennas in black and blue, respectively. Red curves represent linear fits to the data.
Figure 5. (a) Differential reflectivity $\Delta R/R_{\text{off}}$ of a single bowtie nanoantenna encoded in color as a function of excitation polarization angle $\theta$ and energy $E$. (b) Differential reflectivity $\Delta R/R_{\text{off}}$ as a function of energy $E$ for the coupled mode $E_c$ and the uncoupled mode $E_{\text{uc}}$ in blue and green, respectively. Grey symbols represent the degree of linear polarization $\rho = \frac{\Delta R}{R + \Delta R}$ as a function of energy $E$. Red curves show corresponding simulations of both modes. (c) Integrated differential reflectivity as a function of excitation polarization angle $\theta$ for the coupled mode $E_c$ and uncoupled mode $E_{\text{uc}}$ in blue and green, respectively.

recorded from an individual $(N = 1)$ and an ensemble $(N \sim 12)$ of bowtie nanoantennas on a glass substrate in blue and black, respectively. Here, $N$ denotes the number of bowtie nanoantennas excited simultaneously in the differential reflectivity measurements. The left upper and lower insets in Fig. 4(a) show white light microscopy images of the bowtie array with the excitation spot of the white light super-continuum source and a halogen lamp for single and ensemble antenna spectroscopy, respectively. The differential reflectivity spectra $\Delta R/R_{\text{off}}$ for single and ensemble antenna measurements exhibit a maximum at comparable $E_{\text{uc}}$, attributed to the localised surface plasmon resonance. However, the corresponding resonance linewidth $\Gamma_{\text{res}}$ for the measurement of an individual bowtie nanoantenna is found to be considerably narrower as compared to bowtie nanoantenna ensembles, clearly visible on a normalized differential reflectivity scale as shown in the inset of Fig. 4(a). The larger linewidth for the ensemble measurement is attributed to inhomogeneous broadening.

We systematically investigated this effect by determining $\Gamma_{\text{res}}^{-1}$ of individual bowtie nanoantennas with constant $g = 10 \pm 3 \text{ nm}$ as a function of measured triangle size $s$. The results of those measurements are plotted as blue symbols in Fig. 4(b). The red line represents a linear fit to the data, indicating a systematic broadening of $\Gamma_{\text{res}}^{-1}$ for increasing $s$ from $\Gamma_{\text{res}}^{-1} = 0.26 \text{ eV}$ at $s \sim 100 \text{ nm}$ to $\Gamma_{\text{res}}^{-1} = 0.34 \text{ eV}$ at $s \sim 150 \text{ nm}$. This observed increase in $\Gamma_{\text{res}}^{-1}$ is attributed to enhanced radiation damping for increasing antenna sizes. Furthermore, we present for comparison differential reflectivity measurements conducted on bowtie nanoantenna ensembles for nominal sizes $100 \text{ nm} < s_c < 150 \text{ nm}$ with $\Delta s_c = 10 \text{ nm}$ as black symbols in Fig. 4(b). In addition to the linear increase in $\Gamma_{\text{res}}^{-1}$ with increasing $s_c$ due to enhanced radiation damping, we observe a global offset $\Delta \Gamma_{\text{res}} = \Gamma_{\text{res}}^{-1} - \Gamma_{\text{res}}^{-1}$ for the ensemble measurements attributed to inhomogeneous broadening, which varies between $\Delta \Gamma_{\text{res}} = 0.07 \text{ eV}$ and $\Delta \Gamma_{\text{res}} = 0.21 \text{ eV}$ for $s \sim 100 \text{ nm}$ and $s \sim 150 \text{ nm}$, respectively. We note that the unexpected non-constant offset $\Delta \Gamma_{\text{res}}$ for increasing $s$ cannot be explained by the current experiments and requires further experimental and theoretical investigations, which will be presented elsewhere. Altogether our results demonstrate the impact of small variations in triangle size $s$ and gap size $g$ on the localised surface plasmon polariton resonance of bowtie nanoantennas despite the high fabrication accuracy achievable with state-of-the-art nanotechnology.

Finally, we investigate the inter-particle coupling between the localised surface plasmon polaritons in the individual Au triangles, which form the bowtie nanoantenna. Therefore, we performed differential reflectivity measurements on an individual bowtie nanoantenna with $s_c = 140 \text{ nm}$ and $g_c = 10 \text{ nm}$ as a function of the excitation polarization angle $\theta$. Here, $\theta$ is defined as the angle between the electric field vector of the linearly polarized excitation and the long axis of the bowtie nanoantenna, i.e. the y-axis as defined in Fig. 1(a). We show in Fig. 5(a), the differential reflectivity signal $\Delta R/R_{\text{off}}$ of a single bowtie nanoantenna encoded in colour as a function of energy $E$ and excitation polarization angle $\theta$. We observe two energetically separated resonances at $E_c = 1.41 \text{ eV}$ and $E_{\text{uc}} = 1.75 \text{ eV}$ for $\theta = (0^\circ, 180^\circ)$ and $\theta = (90^\circ, 270^\circ)$, respectively, which we attribute to the coupled and uncoupled nanotriangle resonances. The $E_c$-resonance appears at significantly lower energy as compared to the resonance of an individual nanotriangle $E_{\text{uc}}$ due to near-field coupling between the localised surface plasmon polaritons in the two triangles. This finding is in good agreement with similar studies on bowtie nanoantenna ensembles as a
function of gap size \( g \), where increased gap sizes lead to a vanishing of the polarization resolved response, due to decreased interparticle coupling. We support this assumption by numerical simulations of the scattering cross-section \( \sigma \) for a bowtie nanoantenna with \( s_0 = 140 \text{ nm} \) and \( g_0 = 10 \text{ nm} \). We compare in Fig. 5(b) the simulation results dashed for the coupled \( \theta = 0^\circ \) and solid line for the uncoupled mode \( \theta = 90^\circ \), red solid line with the according linewidth and nano-plasmonic concepts for the realization and optimization of efficient optical on-chip nanocircuits60. In conclusion, we believe that our study provides an important step towards the marriage of semiconductor devices requiring transparent substrates. Single-particle spectroscopy using a dark field microscope41 requires immersion oils that contaminate the sample surface and, thus, modifies the optical properties of the plasmonic nanoparticles. In contrast to scanning near-field optical microscopy40, which demands expensive equipment and records information in a serial manner, the demonstrated differential reflectivity spectroscopy method offers quick and direct insights into the main optical properties of bowtie nanoantennas and potentially also works at cryogenic temperatures. The latter property becomes important when coupling plasmonic antennas to optically active emitters embedded in the semiconductor substrates41,43. In combination with the control over the antenna position56 and local electric contacts13, this enables to engineer the spontaneous emission dynamics in such hybrid semiconductor-plasmonic nanosystems via the well-known Purcell-effect17. The enhancement is linked to the resonance linewidth \( \Gamma_{\text{ru}} \) via the so-called quality factor \( Q = E_{\text{ru}} / \Gamma_{\text{ru}} \) and, therefore, nanostructures yielding minimum linewidth are favourable. The obtained Q-factors for the bowtie nanoantennas studied range between 5 and 10 and are in good agreement with studies on chemically synthesized spherical Au nanoparticles41. Additional numerical simulations of truncated bowtie nanoantennas are presented in Fig. SM3, indicating a further improvement of \( \Gamma_{\text{ru}} \) by a factor 1.3–1.5 \( \times \). This is achieved by modifying the triangles of the bowtie nanoantenna to a ‘two-wire gap’-like antenna13,25, giving rise to a reduction of the antenna volume, whilst simultaneously keeping the resonance energy constant. Further improvement of the Q-factor is expected by using single-crystalline metals due to a reduction of Ohmic losses in the metal as recently demonstrated in refs 58 and 59. Finally, it is well known that Ag instead of Au does not only allow to further increase the surface plasmon polariton energy, but also shows promise of decreased losses since the interband transitions are shifted towards higher energies46. In conclusion, we believe that our study provides an important step towards the marriage of semiconductor devices and nano-plasmonic concepts for the realization and optimization of efficient optical on-chip nanocircuits40.

**Methods**

**Sample fabrication and layout.** The samples investigated were defined on semi-insulating GaAs [100] wafers or glass (MENZEL microscope cover slips) substrates. After cleavage, the samples were flushed with acetone and isopropanol (IPA). In order to get a better adhesion of the e-beam resist, the samples were put on a hot plate (170 °C) for 300 s. An e-beam resist (Polyimethylenacrylat 950 K, AR-P 679.02, ALLRESIST) was coated at 4000 rpm for 40 s at an acceleration of 20000 rpm/s and baked out at 170 °C for 300 s; producing a resist thickness of 70 ± 5 nm. For the glass samples, we evaporated 10 nm aluminium on top of the Polyimethylenacrylat layer to avoid charging effects during the e-beam writing. The samples were illuminated in a Raith E-line system using an acceleration voltage of 30 kV and an aperture of 10 μm. A dose test was performed for every fabrication run, as this crucial parameter depends on the varying e-beam current. Typical values were 800 μC/cm² for GaAs and 700 μC/cm² for glass substrates. After the e-beam writing the aluminium layer on the glass samples was etched away using a metal-ion-free photoresist developer (AZ 726 MIF, MicroChemicals). All samples were developed in Methylisobutylketon diluted with IPA (1:3) for 45 s. To stop the development, the sample was rinsed with pure IPA. For the metatisation an e-beam evaporator was used to deposit a 5 nm thick titanium adhesion layer for the glass and 35 nm of gold for all substrates at a low rate of 1 Å/s. The lift-off was performed in 50 °C warm acetone, leaving behind high-quality nanostructures with feature sizes on the order of 10 nm.
Structural characterisation. To determine the geometrical parameters of the fabricated nanoantennas we took scanning electron microscopy images using a Raith E-line system at an electron acceleration voltage of 5 kV and an aperture size of 10 μm. We recorded the pictures by stepping from one antenna to another and conducting a single shot scan in order to avoid charging effects, which occur especially on the glass samples. The obtained images were analysed by hand using the “Carl Zeiss SmartTiff Annotation Editor” (V1.0.1.2). As stated in the main text we extracted s and g from high resolution scanning electron microscopy measurements of ~300 bowtie nanoantennas without any pre-selection. To quantify the tip radius we evaluated 20 “feed-gap tips” of the upper triangle and found a value of $r_s = 1 ± 0.1 \mu m$ and $r_g = 5.2 \mu m$, respectively. The sample were placed on an open-loop piezo stage (Thorlabs NanoMax) in combination with a tiltable path. The reflected light was collected by the same objective, transmitted through the beamsplitter, a fibre coupler and a multimode optical fibre before it was dispersed and analysed in a 0.5 m imaging spectrometer (Princeton Instrument Acton SP2500i, grating: 300 /mm). Both excitation and detection channels were equipped with linear polarizers (Thorlabs, LBVIS100-MP2) and λ/2-waveplates (Thorlabs, AHWP10M-980) mounted on computer controlled motorized sample stages (Thorlabs, PRM1/MZ8) to adjust and analyse the polarization. For the measurements on glass (GaAs) we used a 600 nm (800 nm) long pass filters and a Si-CCD - Princeton Instruments Spec-10 (InGaAs linear array - Princeton Instruments, OMA V). When using the super continuum source to investigate the nanoantennas on GaAs, we also installed a 1064 nm notch filter in order to suppress the residual light from the seed laser, which potentially can damage the InGaAs detector. To cover the broad energy range discussed in the main part of this work, we always recorded four spectra of different centre energies, which were merged afterward. The integration time was always set to 1 s.

Optical spectroscopy. For optical spectroscopy we used either a white-light super-continuum source (Fianium WhiteLase micro) for single particle studies or we collected and collimated the light from a halogen lamp (Philips Fibre Optic Lamp, Type 6423 XHP FO) for ensemble measurements. Both beams were sent through a beamsplitter and an apochromatic high numerical aperture (NA = 0.9) objective to focus the light onto the sample surface. We determined the spot sizes to be $\theta_{spot} = 1 ± 0.1 \mu m$ and $\theta_{halogen} = 5.2 \mu m$, respectively. The sample were placed on an open-loop piezo stage (Thorlabs NanoMax) in combination with a tiltable path in order to provide an accurate positioning and an exact alignment of the plane perpendicular to the optical path. The reflected light was collected by the same objective, transmitted through the beamsplitter, a fibre coupler and a multimode optical fibre before it was dispersed and analysed in a 0.5 m imaging spectrometer (Princeton Instrument Acton SP2500i, grating: 300 /mm). Both excitation and detection channels were equipped with linear polarizers (Thorlabs, LBVIS100-MP2) and λ/2-waveplates (Thorlabs, AHWP10M-980) mounted on computer controlled motorized sample stages (Thorlabs, PRM1/MZ8) to adjust and analyse the polarization. For the measurements on glass (GaAs) we used a 600 nm (800 nm) long pass filters and a Si-CCD - Princeton Instruments Spec-10 (InGaAs linear array - Princeton Instruments, OMA V). When using the super continuum source to investigate the nanoantennas on GaAs, we also installed a 1064 nm notch filter in order to suppress the residual light from the seed laser, which potentially can damage the InGaAs detector. To cover the broad energy range discussed in the main part of this work, we always recorded four spectra of different centre energies, which were merged afterward. The integration time was always set to 1 s.

Simulations. We simulated the scattering cross-sections of the bowtie nanoantenna using a commercially available finite difference time domain solver (Lumerical Solutions, Inc., FDTD solutions, version: 8.11.387). The design of the simulation cell is based on the Mie scattering tutorial that can be found on the Lumerical homepage. Consequently, we used a three dimensional simulation cell that is terminated by perfectly matched layers. The bowtie was modelled using the extruded triangle and found a value of $\lambda_{spot} = 4 ± 0.1 \mu m$ of the upper triangle. The used simulation file is available in the supplementary material.

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Author Contributions

The authors declare no competing financial interests.

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