# Supplementary data to

# Enhanced plasmonic properties of gold-catalysed semiconductor nanowires.

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## S1. Sonication of ZnSe NWs in isopropanol and transfer to the glass coverslips

As-grown ZnSe NWs of various lengths in the range of 0.45-1.7  $\mu$ m on GaAs(111)B substrates of 10 mm<sup>2</sup> area each were placed into the 2mL microcentrifuge tubes (Primo boil-proof microcentrifuge tubes, EuroClone) and immersed in 500  $\mu$ L of isopropanol (J.T.Baker®). Then the tubes were placed into the ultrasonic bath (35 kHz, 320 W, Bandelin Sonorex Digitec DT100H) and sonicated for 30 sec. The GaAs wafers were removed from the solutions and a few droplets (3  $\mu$ L each) were placed either onto the preliminary cleaned glass coverslips (0.15 mm thick, Bio Optica) to be characterized by UV-vis spectroscopy or onto Silicon wafer for SEM characterisation. As it is seen from the Fig S1c this approach allows to remove the NWs from the substrate, however the length of removed NWs is shorter as at least 20% compared with as-grown wires. When deposited onto the Silicon or glass coverslip they tend to aggregate.



**Figure S1.** (a, b) SEM images of as-grown 1.7 μm long ZnSe NWs on GaAs(111)B substrate, (c) the sample after sonication and (d) transferred ZnSe NWs from isopropanol solution onto Si substrate.

### S2. Simulation of extinction spectra

The simulations were performed in COMSOL Multiphysics 4.2 software using Mie theory [S1, S2]. The optical constants of the gold are taken from [S3], while ZnSe and GaAs ones are from [S4] and [S5], respectively. Figures S2a and S2b show the calculated extinction spectra of gold NPs as a function of increased size of NP (a) or dielectric permittivity of environment (b). In both cases the peak position of plasmon resonance is red-shifted, and moreover, becomes broader. Here the extinction is determined by the absorption for a broad range of NP size. In case of gold-catalysed NWs with a diameter less than 50 nm the absorbance is still dominating on the scattering (Figure S2d), while the shape of absorbance curve becomes complex. In our experiment (Figure 3a in the main text), gold-catalysed ZnSe NWs were transferred onto the glass coverslips. Since we used a halogen source, the light was unpolarized. Therefore, in the simulations we considered a perpendicular or parallel polarization of the light in respect to the NW axis (Figure S2e). The averaged spectra for these two border cases are displayed in Figure S2d. It is clearly seen the presence of two peaks caused by significant difference in the dielectric perceptivities of air and ZnSe. In fact, the plasmon peak should be located in between those two peaks.



**Figure S2.** (a, b) The calculated extinction spectra of individual gold NPs in various media based on Mie theory. The parameters of calculations, diameter of NP and dielectric permittivity, are shown in the legend. (c) The distribution of electrical field for gold NP with diameter of 30 nm in air at the excitation wavelength of 540 nm. (d) The calculated absorbance and scattering spectra of gold-catalysed ZnSe NWs. The displayed spectra have been obtained as an average of two cases with a polarisation shown in (e). (f) The distribution of electrical field for gold-catalysed ZnSe NW with diameter of 30 nm in air at the excitation wavelength of 540 nm. The orientation of electrical field for gold-catalysed ZnSe NW with diameter of 30 nm in air at the excitation wavelength of 540 nm. The orientation of light polarisation in (c, f) is shown in the image.

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## S3. Metal-free NWs

## S3.1 Etching of gold NPs of ZnSe NWs in Ar<sup>+</sup> plasma

As grown ZnSe NWs onto GaAs substrates had been etched in Ar<sup>+</sup> plasma reactor (Kenosistec Srl) at voltage bias of 400 V, RF power of 200 W, Ar flux of 20 sccm, and pressure of 0.3 mbar. It was observed that an optimal etching time to remove gold is about 4 min at mentioned parameters. A further increase of etching time leads to significant changes in the NW diameter and shape.





Etched in Ar<sup>+</sup> plasma for 4 minutes



**Figure S3.1.** Tilted and cross-sectional SEM images of as grown (top) and etched in Ar<sup>+</sup> plasma for 4 minutes (bottom) ZnSe NWs on GaAs(111)B substrate. The transferred individual NWs are shown in the centre of image clearly demonstrating the absence of gold at the end of wire.

## S3.2 Self-catalysed GaAs NWs

GaAs NWs were grown using Ga droplets as metal particle catalyst. At the end of the growth the sample was exposed to As flux only in order to transform the Ga particle in GaAs. The resulting wires are made only of semiconducting material.



**Figure S3.2.** Tilted SEM images of as grown self-catalysed GaAs NWs on GaAs(111)B substrate. The insets show an absence of metal particles at the tops of NWs while the GaAs crystalline facets at the ends of NWs are clearly seen.

### S4. Photoluminescence on ZnSe NWs

Low-temperature photoluminescence measurements (Figure S4a) were performed at 14 K and excitation wavelength of 375 nm. 100 nm thick ZnSe bulk crystal epitaxially grown on GaAs(100) at 280°C and further annealed at 450°C for 10 minutes and as-grown (450°C) ZnSe NWs were characterised. The annealed bulk ZnSe crystal demonstrates few narrow peaks in the near band edge (NBE) region, 440-465 nm, ascribed to the free and bound exciton recombinations at 2.73 and 2.80 eV [S6]. Two broad bands at lower energy, centred at 2.30 and 1.99 eV, respectively, are also observed. It is known that high growth temperatures or thermal treatments after the growth are detrimental for ZnSe crystals, inducing the formation of point defects, which are a cause of deep level (DL) recombination within the band gap [S7, S8]. In particular, DL states localized at the ZnSe/GaAs interface have been reported [S9, S10] and have been attributed to Ga impurities on Zn sites associated with nearby Zn vacancies [S11].

The growth of Au-assisted ZnSe NWs on GaAs substrates at 450°C is triggered by Au-Ga alloy nanoparticles, and Ga atoms are released from the nanoparticle during the growth, through the so-called self-purification mechanism as discussed in the main text. The presence of Ga impurities all along the wires' body can explain the predominance of DL emission in the PL spectrum of the wires. Moreover, Au-atom incorporation in ZnSe NWs grown at 450°C has been demonstrated [S12], and Au impurities into ZnSe crystals also can induce DL states within 1.8 and 2.2 eV [S13].

Note that we used two different setups for low-temperature photoluminescence measurements and Raman characterisation. Thus, a 375 nm beam was slightly focused on the sample by low NA objective and excited a big area of it. Therefore, a DL signal is partially proportional to the volume fraction of ZnSe and it is higher for longer wires.

Using a 532 nm excitation only the emission from DL can be observed. This is the cause of the observed PL background signal in ZnSe NWs Raman spectra (Figure S4b). When a 532 nm laser beam is focused by 40x objective onto the tops of ZnSe NWs similar Raman spectra are obtained. The PL background does not depend neither on NWs length nor existence of gold NPs, corresponding about the same level of DL emission from ZnSe NWs. The increased PL background in case of 100 nm thick ZnSe bulk crystal in Figure S4b is due to higher volume fraction of ZnSe at the focal plane. Moreover, its crystalline structure along with a contribution from GaAs substrate is the cause of the observed broad Raman peak centred at 500 cm<sup>-1</sup>, which is due to the combination of TO and LO Raman modes of ZnSe and GaAs [refs 38-40 in the main text] or their overtones.



**Figure S4:** (a) PL spectra of bulk ZnSe crystal grown at 280°C on GaAs(100) substrate and then annealed at 450°C, and two kinds of gold-catalysed ZnSe NWs of 400 nm and 950 nm long excited at 375 nm wavelength at 14K. (b) Raman spectra of ZnSe NWs when 532 nm laser beam is focused onto the gold NPs.

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#### S5. B3g Raman mode of pentacene as an indicator of molecule orientation

Figure S5 displays the B<sub>3g</sub>/A<sub>g</sub> ratio taken at 1596 cm<sup>-1</sup> and 1371 cm<sup>-1</sup> as a function of ZnSe NW length. Reference ratios are also displayed with different colours for glass and polycrystalline Au film. The intensity of B<sub>3g</sub> mode depends on the orientation of pentacene molecule with respect to the polarization of incident laser excitation [S14, S15], which in our experimental configuration is parallel to the substrate and perpendicular to the NWs (Figure S2d). It is expected to reach a maximum on flat gold for planar light polarization, indicating that pentacene molecules are lying flat on the surface [S16]. The ratio shown in Figure S6 is constant around 0.4 within the error, with the only exception of the shortest NWs for which is 0.25, whereas on polycrystalline gold film (horizontal orientation of the molecule) we measured 0.85, twice higher value than on NWs. This value on glass substrate is less than 0.1 (vertical orientation). The difference in ratio numbers can be explained by different geometry of pentacene adsorption on flat gold surface and spherical NPs as shown in Figure S8. These data are consistent with the hypothesis that the most of the Raman signal come from the molecules which are oriented approximately at 45 degrees with respect to polarisation of the light.



Figure S5. B<sub>3g</sub> to A<sub>g</sub> modes ratio as a function of ZnSe NWs length.

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S6. Statistical characterisation of gold NPs formed on flat GaAs(111)B substrates by the annealing and the change of density of plasmon-active sites with a length of NWs



**Figure S6.1.** (a) Typical top-view SEM image of gold NPs onto the flat GaAs(111)B substrate formed by the annealing in vacuum of 5 monolayers gold film (1 nm thick). (b) An example of NPs lateral size estimation by Gwyddion 2.33 software. (c) Size distribution of NPs averaged from 5 SEM images. The averaged density of gold NPs on flat GaAs(111)B substrate is 120 per  $1 \mu m^2$ , a mean diameter is 33.3 nm.

When the ZnSe NWs are being grown the density of vertically oriented ones (or number of plasmonic sites at the focal plane) is decreased with their length (growth time). This is mostly due to stacking or kinking during growth (Figure S6.2). The mean diameter of gold particles at the end of vertically aligned ZnSe NWs is slightly decreasing down to 20 nm for the longest wires used in this work (1650 nm length). Depending on the geometry and size of tested materials (planar micrometer size GO flakes or pentacene molecules) the fractional area occupied by gold (coverage) should be considered.



**Figure S6.2.** (a, b) SEM images of 400 nm and 900 nm long gold-catalysed ZnSe NWs on GaAs(111)B with respective statistical data obtained by means of Gwyddion 2.33 software. (c) Summarized length dependent characteristics of percentage fractional area occupied by gold at the focal plane of laser beam (d). (e) Statistical characterisation of 1 µm long gold-catalysed GaAs NWs.

#### S7. GO Raman response on Au-catalysed ZnSe NWs

The G-peak of graphite is due to optical  $E_{2g}$  phonons at the Brillouin zone center and it is caused by bond stretching of  $sp^2$  carbon atoms in both rings and chains. It becomes broader with an increase of disorder in the graphitic material. The D peak is due to the breathing mode of rings and requires a defect for its activation, it increases therefore with a disorder and could be also a criterion of relative number of  $sp^3/sp^2$  hybridized atoms presented as D/G ratio [S17-S19]. Typically, D/G≈1 for GO fabricated by Hummers method, D=0 for high-quality graphite or ideal graphene sheet (only trigonally bonded  $sp^2$  atoms, G at 1580 cm<sup>-1</sup>), and vice versa, G=0 for diamond crystal (only tetragonally bonded  $sp^3$  atoms, 1332 cm<sup>-1</sup>).



**Figure S7.** Raman spectra of GO flakes deposited onto the gold-catalysed ZnSe NWs reflecting an increase of GO Raman response with increase of number of stacked flakes. The averaged Raman spectrum from single-layer GO flakes is shown in black colour while the spread in averaged spectra is displayed in grey.

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# S8. Deposition geometry of the used analytes on ZnSe NWs

Schematic view of GO on NWs



Figure S8. The schematic view of GO and pentacene orientation with respect to plasmonic field of Au NP at the end of goldcatalysed ZnSe NW.