Coupling Colloidal Quantum Dot Supraparticle Microlasers with Surface Plasmon Resonances via Plasmonic Gold Substrates

Isaac Noman*, Charlotte Eling, Pedro Alves, Nicolas Laurand*
Institute of Photonics, University of Strathclyde, SUPA

Abstract

The miniaturisation of semiconductor lasers to the nanoscale is difficult because of increasing losses as the laser cavity size approaches the wavelength of light, with some recent efforts focusing on high-refractive index dielectric materials and plasmonics to try and overcome this challenge. With this in mind, we immobilize $CdSe_{1-x}S_x$/ZnS colloidal quantum dot (CQD) supraparticle (SuP) microlasers onto gold nanoparticle (AuNP) coated glass substrates. We study the interaction of the absorption, the non-resonant luminescence, and the whispering gallery modes (WGMs) of SuPs with the localised surface plasmon resonances (LSPRs) of a AuNP substrate. This interaction produces an increase in LSPR peak intensity of 10%. The luminescence and the WGM-to-non-resonant-luminescence ratio are both significantly increased (x2) under continuous wave excitation at the LSPR wavelength. Individual SuPs can also still act as microlasers when pulsed optically pumped on AuNPs outside the LSPR at 355 nm. These findings suggest this platform as a candidate for further development towards electrically driven cw optical energy sources, presenting us a solution processable route to device miniaturisation.

Keywords: Colloidal Quantum Dot, Surface Plasmon Resonance, Whispering Gallery, Gold Nanoparticles, Bottom-Up Self-Assembly, Si-PICs, Biosensor, Chip.

1. Introduction

Over the past two decades on-chip tasks have become increasingly diversified, placing greater stress on current silicon-based photonic integrated circuits (Si-PICs) to produce advanced multi-functionalities from smaller and smaller device architectures.[1,2] Evermore diminutive devices are motivated by improved efficiencies and reduced power consumptions critically needed for future applications. On-chip light sources in the near-infrared and the visible are key components for this, with merits on their integration into Si-PICs including the realisation of AI, data-storage, biosensing, and data-communication modalities for these systems.[2,3] Unfortunately, widely used semiconductor laser technologies suffer from the diffraction limit, which prevents the fabrication of truly nanosized lasers. With the advent of laser cavities that combine semiconductor nanomaterials and dielectrics with metals, progress was made towards miniaturisation, with some of the smallest all-semiconductor light sources coming from these architectures.[4-6]

Recently, our group and others have demonstrated supraparticles (SuPs) composed of nanosized colloidal quantum dots (CQDs), self-assembled from the bottom-up, capable of sustaining laser oscillations due to the high confinement of whispering gallery modes (WGMs) in these gain material structures.[7-9] SuPs are attractive as they are entirely solution-

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processable, have a relatively high refractive index, and are present as colloidal dispersions enabling ease of further device integration. However, CQD SuPs do still experience a size-related constriction on their ability to lase. In the case of CdSSe/ZnS CQD SuPs for example, we typically no longer see lasing below a size of ~ 1 μm because of increasing diffraction loss and the difficulty to efficiently pump such structures.

Thin metals offer a potential solution to this size-based constraint. They can support surface-plasmons, coherent oscillations of conduction electrons, which can be excited by an optical pump source to resonate and produce surface plasmon resonances (SPRs). A nanostructured metal can constrain these down to so-called localised surface plasmon resonances (LSPRs). LSPRs have garnered much interest for nanoscale lighting, circumnavigating the diffraction limit we encounter with semiconductors and dielectrics in general. This has been explored as a route to reduce the mode volume of the electromagnetic field surrounding WGM resonators.[10] For this, a material capable of optical gain to overcome the absorption loss from the plasmonic nanoparticles can be placed in close proximity (<10 nm) to a metallic nanoparticle.[11] Crucially, surface plasmons have no size-based limit on their ability to concentrate optical-energy and therefore have the potential to overcome the size-constraint barrier to nanoscale optical sources.

Herein, inspired by these hybrid plasmonic/semiconductor approaches, we propose to couple CQDs SuPs capable of gain and AuNPs capable of concentrating optical radiation through their LSPRs.[12] For this, we fabricate plasmonic substrates made of glass coated with AuNPs and deposit CQD SuPs on their surface. The overall emission and the WGM-to-luminescence pedestal contrast of the SuPs are found to be enhanced by the AuNPs LSPRs when pumped on-resonance (at 532 nm) with the LSPR. Moreover, the laser performance of these SuPs when pumped off-resonance (at 355 nm) with the AuNP LSPR is not significantly reduced. These are indications of coupling between the SuPs and AuNPs. While this is a first step as the SuPs are micron-size, it presents us with a solution-processable platform that could be capitalized on in order to reduce the size of semiconductor lasers, and to develop more efficient photonic sensing systems.

2. Methodolgy

DI water was purified using a Millipore system. CdS_xSe_{1-x}/ZnS core/shell CQDs (λ = 630 nm) were purchased from CD Bioparticles at a concentration of 50 $mgmL^{-1}$ suspended in toluene. Polyvinyl alcohol (PVA) (13,000 – 24,000 $gmol^{-1}$), chloroform, (3-Aminopropyl)triethoxysilane (APTES), gold (III) acetate, and sodium citrate dihydrate were purchased from Sigma Aldrich and used as supplied. Propan-2-ol and ethanol were purchased from VWR Chemicals.

CQD SuP Fabrication

The supraparticles were fabricated using an oil-in-water (O/W) emulsion templating technique. First, CQDs-in-toluene (50 $mgmL^{-1}$, 100 μL) were precipitated out of suspension by addition of 100 μL of methanol (1:1 vol ratio) after vortexing for 2 minutes to encourage this. The cloudy mixture was then centrifuged (12500 rpm, 10 minutes) to settle the CQDs out of solution, the supernatant was removed, and to reduce any residual solvent, samples were vacuum desiccated for 2 hours. Dried CQDs were dissolved in chloroform to produce a solution of concentration of ~50 $mgmL^{-1}$, to ensure the CQDs were fully re-dispersed we sequentially sonicated and vortexed the Eppendorf's 3x. To produce the emulsion, we combined our CQD solution (50 $mgmL^{-1}$) with PVA (6 $mgmL^{-1}$) in DI water (1:4 V:V ratio), this mixture was emulsified by

continuous vortexing for 5 minutes. The emulsion was then left to stir (400 rpm), aliquots were taken to evaluate progress of toluene evaporation, once sufficient time had passed (typically 4 – 5 h) the stirring was stopped, the resulting SuPs settled out of suspension (8000 rpm, 4 min), washed 2x with water (centrifugation at 8000 rpm, 4 min) to remove any excess PVA, and re-dispersed into 20 vol% IPA.

AuNP Synthesis

AuNPs were synthesised from gold (III) acetate and sodium citrate dihydrate using a technique adapted from Jenkins.[13] A two-step seed mediated process was used to prepare 60 nm gold colloids. The first step involves the reduction of $HAuCl_4$ with sodium citrate by the Frens' Method.[14] Briefly, 1060 μL of Au(III) acetate (0.0254 M) solution was brought to a boil in 99 mL of deionized (DI) water while stirring. Once boiling, 1 mL of sodium citrate (38.8 mM) solution was added. After 15 minutes, the solution was allowed to cool to room temperature. 4 mL of the as-made nanoparticle solution synthesized in step one was added to 52 mL of DI water. The seeds were stirred at room temperature for one hour with 1 mL sodium citrate (38.8 mM), and 900 μL Au(III) acetate (25.4 mM). These growth suspensions were then left to stand at ~4 °C for 2 days before use to allow gradual growth of gold nanoparticles, the resulting suspensions were ~0.2 $mgmL^{-1}$. The nanoparticles were 60 nm in diameter with a standard deviation of 5 nm, measured with a scanning electron microscope (JEOL JSM T100).

Self-Assembled AuNP Layers

Substrates were prepared using commercially available glass microscope slides by drop-casting suspensions of as-synthesised AuNPs in water (~0.2 $mgmL^{-1}$) onto glass microscope slides and drying at 80 ℃ for 10 minutes.

UV-Vis Spectroscopy for LSPRs

The absorbance of CQD materials and prepared substrates were recorded using UV-Vis spectrometry (Thermo Scientific, GENESYS 30 Visible Spectrometer), and plotted to check for overlap with SuP emission and the presence of LSPRs.

Characterisation of the Spectral Emission of Supraparticles – CW on Resonance Pumping

The optical emission from these hybrid systems was recorded by pumping at the LSPR using a continuous wave 532 nm laser (Thorlabs, 532 nm DPSS, DJ532-10) with an optical output power of 10 mW. A spectrometer was used to collect the photoluminescence (PL) from samples set at 90 degrees to the laser diode to avoid background light from the excitation source, with a 540 nm filter in place to further reduce this. The sample was mounted at 45 degrees to the detector and in-line with the laser. Laser light incident on the sample was of a spot-size ~200 μm in diameter and irradiated ensembles of SuPs.

Pulsed Excitation for Microlaser Characterisation – Off Resonance Pumping

Samples of SuPs produced directly on glass slides and AuNPs were used as prepared. The samples were then optically pumped with a 355 nm, 5 ns pulsed, Nd:YAG laser at a 10 Hz repetition rate and a beam spot size of $2.6 \pm 1.5 \times 10^{-5}$ cm^2 . The beam intensity was controlled with a neutral density filter wheel and focused with an objective lens (Nikon 10x/0.25NA). A spectrometer (Avantes AvaSpec-2048-4-DT) with a resolution of 0.57 nm between 200 and 1100 nm and 0.4 nm between 420 and 653 nm was used to acquire the spectra. The integrated emission (Spectral Intensity) versus the pump energy (the laser transfer function) was obtained from this data, with the non-resonant background PL (i.e. PL not coupled to the WGMs) subtracted. The same set-up also allowed imaging of the sample through the objective lens.

3. Results and Discussion

Assessment of SuPs and AuNPs Spectral and Structural Properties

The resulting spectral properties of our samples are reliant upon the spectral overlap between the CQDs structurally constituting the SuPs, the SuPs themselves, and the LSPRs of the AuNP substrate. These can be elucidated by measuring their absorption and emission spectra to compare their overlap, as can be seen in Fig. 1.

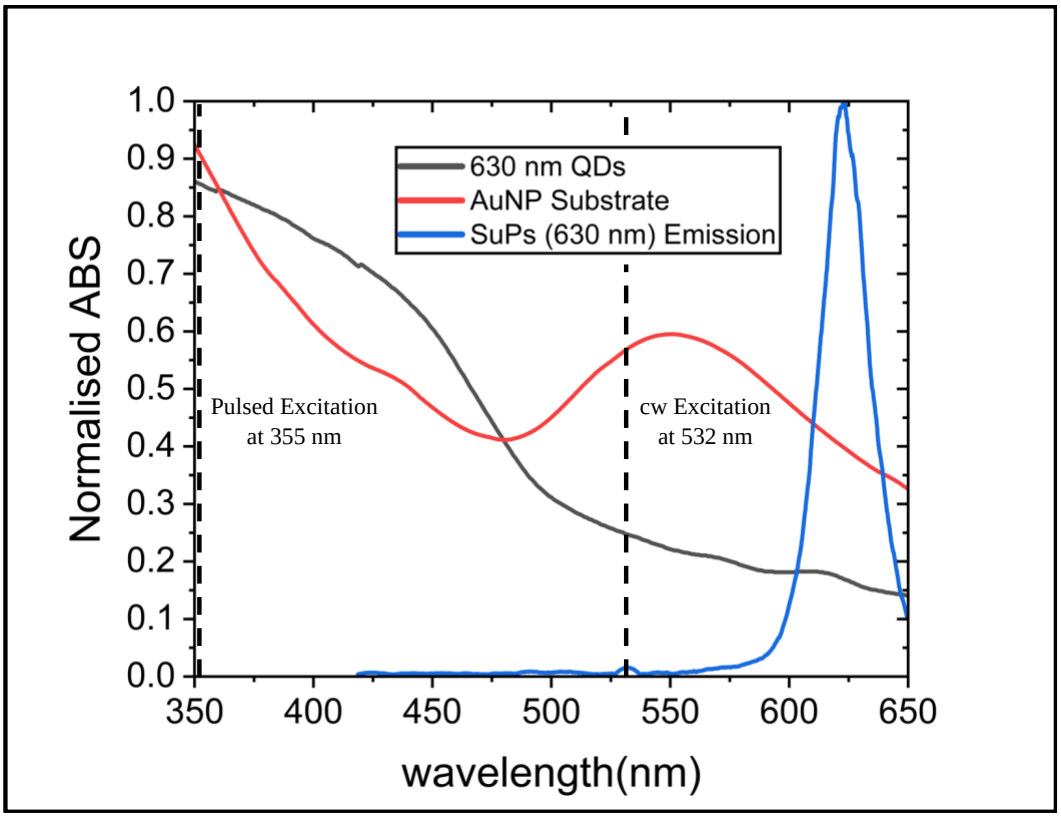

Figure 1. Curves plotted for (black) 630 nm CQD absorption, (red) SPR peak of AuNP substrate, and (blue) emission of our SuPs on glass when irradiated with a 532 nm CW laser. Dotted lines indicate wavelengths at which our SuPs were excited, (pulsed at 355 and CW at 532 nm).

We see that the emission of the SuPs does not overlap well with the SPR of the AuNP substrate (it is 75nm red-shifted), nor does the absorption of the CQDs. The 355 nm pulsed laser utilised as the pump for the study of the lasing characteristics of SuPs (section 3.3) is itself well out of resonance. The continuous wave (CW) excitation laser used for the PL study (section 3.2) though is, at 532 nm, almost on-resonance with the LSPR. We come to observe that these have implications for the properties of the luminescence retrieved from the SuPs, these will be discussed later. In Fig. 2 we show images of a AuNP substrate onto which a suspension of SuPs was drop-cast.

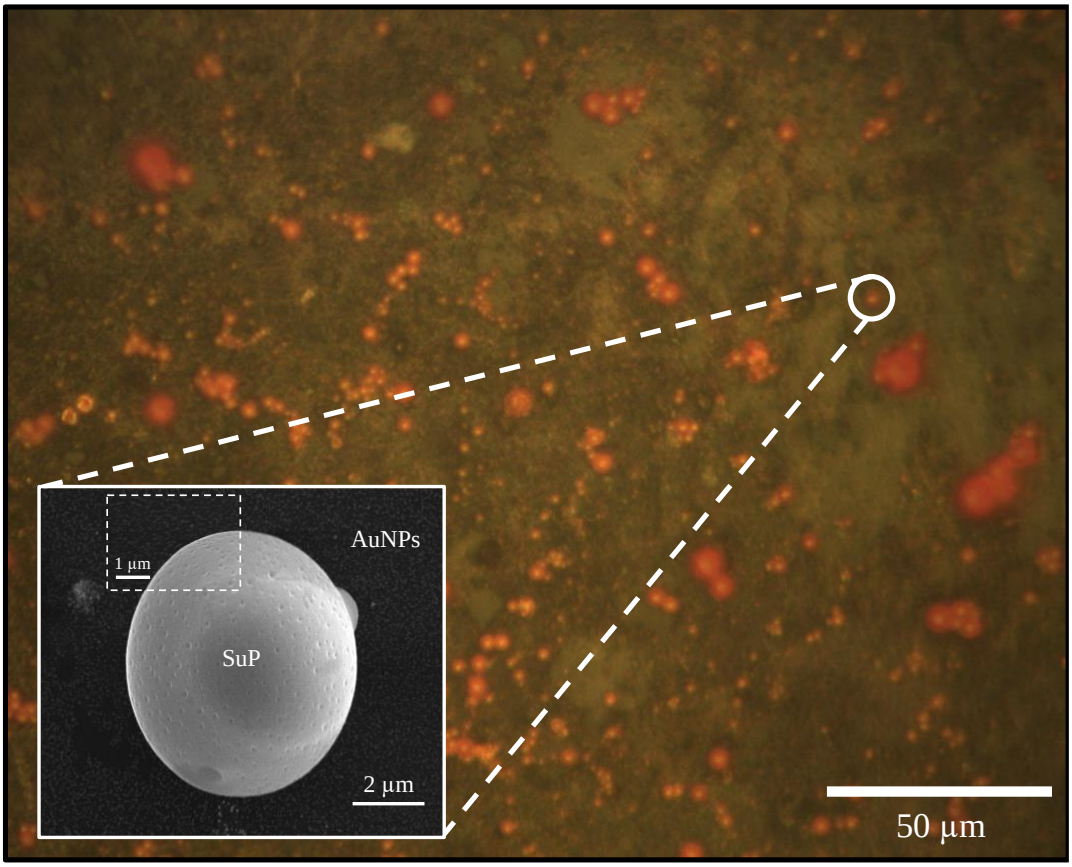

Figure 2. (a) Image of CQD-SuPs (λ = 630 nm) deposited by drop-casting from suspension in 20% (vol) IPA. Inset is a SEM image of a SuP on a glass substrate.

As we can see in Fig. 2 there is a relatively homogenous coverage of AuNPs and SuPs within our samaple. This suggests when undertaking CW luminescence studies, we will be illuminating ensembles of these SuPs to characterise an average sample response; whereas, when using pulsed excitation, we will excite individual SuPs to characterise their thresholds. To understand the spectral overlap of our sample when interrogating with both methods of excitation (CW at 532 and pulsed at 355 nm), we collect absorption data for our samples, these are presented in Fig. 3 below.

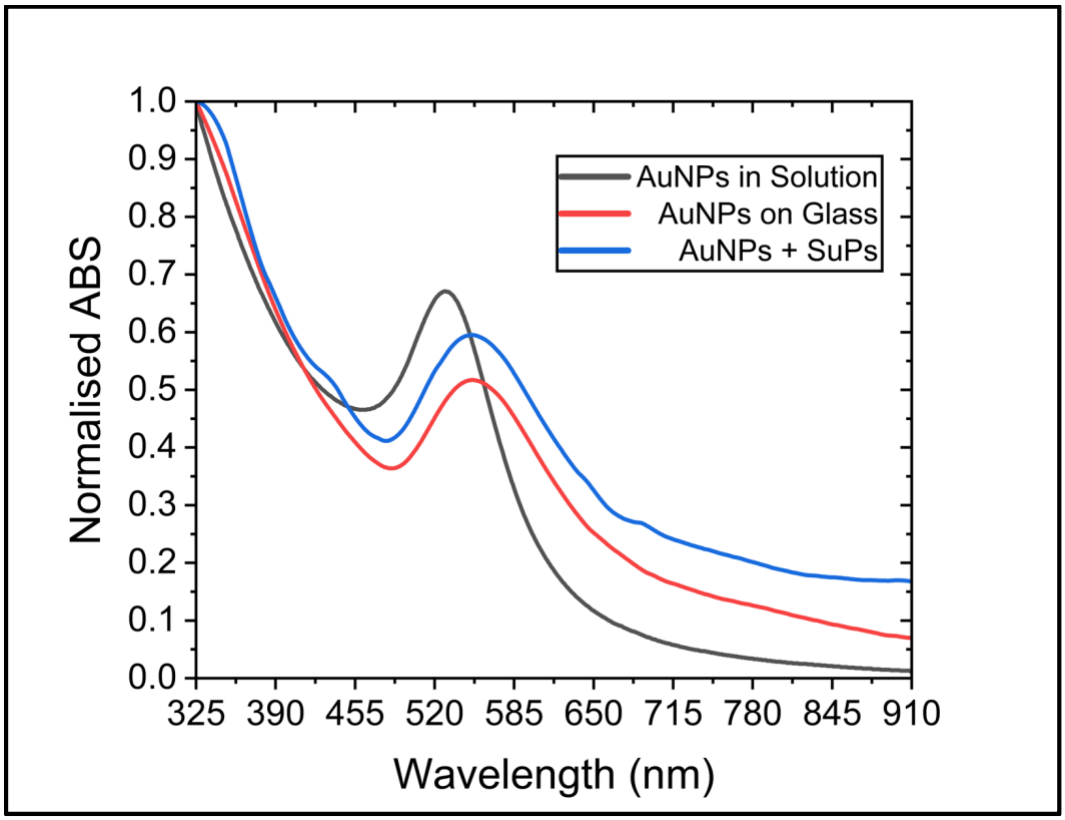

Figure 3. Absorbance spectrum for AuNPs (black curve) in solution ~ 0.2 mgmL^{-1}, (red curve) once drop-cast onto glass without SuPs, and (blue curve) with SuPs.

We clearly see a strong peak around 530 nm in Fig. 3, indicating the presence of LSPRs from the AuNPs on glass. Compared to the AuNPs in solution, the absorbance of the AuNPs on the glass substrate appears broader which could suggest the generation of some small nanoparticle aggregates during substrate coating. This, likely a function of the convective and Marangoni forces experienced by the particles driving them towards one another and the contact line of our suspension droplet, encouraging their nucleation by van der Waals interactions. When added to the surface of the AuNP substrate, the SuPs cause an increase of around 10% in LSPR peak intensity, as well as a broadening of the LSPR band suggesting weak coupling between SuP WGMs and AuNP LSPRs. To better understand the behaviour of SuPs when onto a AuNP substrate we progress to evaluate their emission properties.

Enhancement of SuP WGM luminescence by AuNPs

To investigate the capability of the AuNP substrates to enhance the emission of CQD SuPs, we used a CW green laser (λ = 532 nm) to excite ensembles of SuPs on both glass and AuNP coated substrates. Results are summarized in Figure 4.

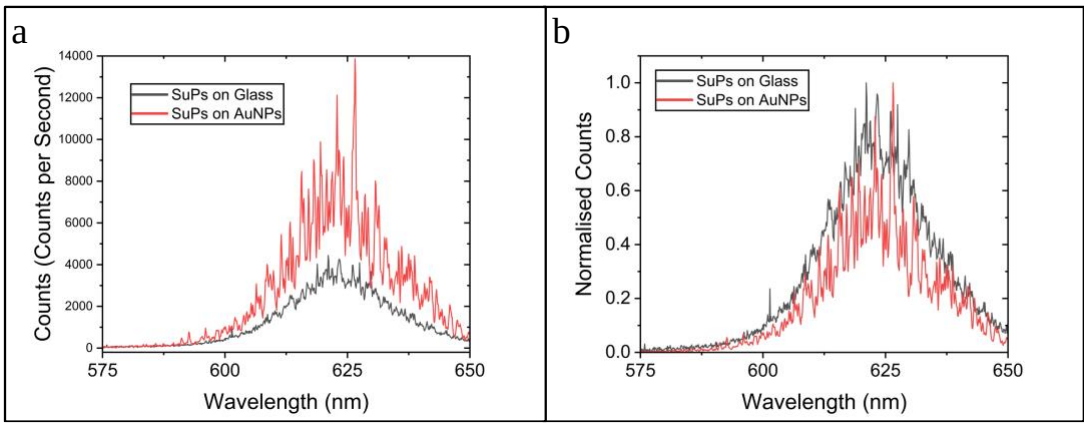

Figure 4. Spectra recorded for (a,b) SuPs on a AuNP substrate and on bare glass, curves in (b) were normalised to highlight the sharper mode features present for the AuNP samples. Spectra were collected at an optical output power of 10 mW. The size distribution of the SuPs tested here were 3.1 ± 1.8 μm.

The emission is made of background luminescence (i.e. photon not coupled to WGMs of the SuPs) and luminescence from the WGMs. The latter is characterised by narrow peaks which are superposed on top of the broader background PL pedestal. The emission in this case is from an ensemble of SuPs, each supporting several WGMs. As seen in Fig. 2, the SuPs deposited on the substrate have a relatively high density and we can approximate the emission spectra as the sum of the contributions from each individual SuP. It is clear that the contrast between the WGMs and the luminescence pedestal is stronger when the SuPs are on AuNP substrates, by approximately a factor of 2. The overall luminescence pedestal is also increased by a factor of 2. We measure the full width at half maximum (FWHM) of the WGM peaks, allowing us to compute estimations for cavity Q-factors in these hybrid systems. Q-factor up to ~1400 is seen (non-slit limited, resolution of spectrometer = 0.13 nm), which is high for a self-assembled system,[7,15] where shape and overall homogeneity of the cavity is enforced by emulsion droplet surface-tension, quantum dot concentration, and the drying conditions. Particularly pertinent is the enhancement of our WGMs by the AuNPs, WGMs are near absent for the SuPs on glass, whereas well-defined peaks are present in the AuNP sample. The enhancement of luminescence from the sample is likely a result of the combination of absorbed pump photons, which are resonant with the LSPR, and scattering from the AuNPs.[16]

Performance of SuP Microlasers

Importantly, for work towards nanoscale lasers, and for possible applications in visible wavelength PICs, the ability of SuPs to sustain laser action without significant degradation on AuNP substrates is important. We give the laser characterization of SuPs on glass and on AuNPs in Fig. 5 below.

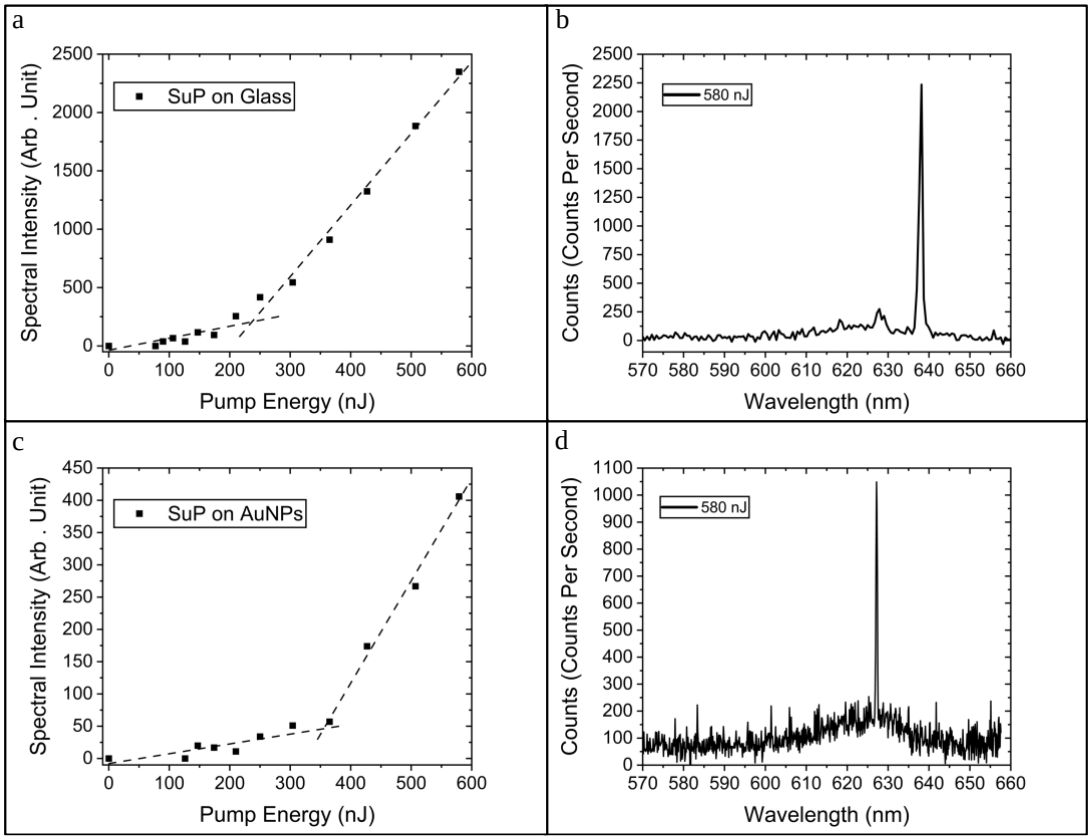

Figure 5. (a,c) laser transfer functions (LTFs) and (b,d) emission spectra of SuPs on (a,b) glass and (c,d) AuNPs. Dashed lines indicate fits used to determine SuP thresholds from the LTFs.

The threshold of our SuP on glass (~3 μm) is 270 ± 30 nJ, whereas on AuNPs (~4.5 μm) it is 397 ± 67 nJ a difference of approximately 47%. While this difference is significant for these two samples, a full statistical analysis is needed to elucidate if this difference is indeed caused by the different substrates or from possible differences in SuP homogeneities or qualities. The count difference between Figs 5a and 5c and between Figs 5b and 5d is due to the collection of data from separate detection channels having different sensitivity. For the SuPs on glass, we did not retrieve sufficient emission intensity to characterise them with greater resolution, although this means a greater signal at detection when compared with the SuPs on AuNPs recorded at greater resolutions. The possibility of using a higher resolution channel for the SuPs on AuNPs comes from the enhancement of the SuP emission like we have seen on ensembles when pumping near the LSPR, even though here we pump out of resonance Moreover, the difference in linewidth between the two samples (SuP on glass = 3.5 nm, SuP on AuNPs = 1 nm) can be attributed to this difference in resolution, as the lack of resolution in 5b.. Crucially, even if the increase in threshold is due to the substrates, the SuPs are still able to sustain laser oscillations when on AuNPs and with reasonable thresholds.

4. Conclusion

We have shown that SuP WGM cavities can interact with a AuNP coated substrates LSPRs. These interactions lead to several changes in the SuPs performance; their luminescence under cw excitation is greatly enhanced by over 2-fold when excited almost on-resonance with the LSPRs while the contrast between WGMs and the luminescence pedestal doubles. Individual SuPs can still act as microlasers when on AuNP coated substrates and the overall emission is also increased compared to SuPs on bare glass. The threshold on the tested sample also increases by 47% when excited off-resonance with AuNPs LSPRs, although further investigations are needed to elucidate if this is from the substrate or simply from statistical variation between different SuPs. We believe this system could be optimised to produce arrays of nanoscale optical concentrators, capable of becoming on-chip light sources which are both solution processable, and compatible with self-assembly techniques. In future works we would be interested in evaluating the difference in optical properties when using SuPs that emit roughly at the LSPR wavelength of our AuNPs, this could be pre-cursory to producing a spaser architecture or a lasing spaser in our system.

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References

1. Z. Zhou, B. Yin, J. Michel, "On-chip light sources for silicon photonics" Light. Sci. Appl. 4(358), (20th November 2015), https://doi.org/10.1038/lsa.2015.131
2. J. Yang, M. Tang, S. Chen, H. Liu, "From past to future: on-chip laser sources for photonic integrated circuits" Light. Sci. Appl. 12(16), (15th January 2023), https://doi.org/10.1038/s41377-022-01006-0
3. Z. Zhou, X. Ou, Y. Fang, E. Alkhazraji, R. Xu, Y. Wan, J. E. Bowers," Prospects and applications of on-chip lasers". eLight. 3(1), (4th January 2023), https://doi.org/10.1186/s43593-022-00027-x
4. W.-S. Cheung, I.-T. Huang, Z. Y. Wu, P.-Y. Chang, H.-C. Hsu, Y.-P. Lan, Y.-H. Chou, "Advancements in nanoscale coherent emitters: The development of substrate-free surface plasmon nanolasers" APL. Photon. 9(016103), (4th January 2024), https://doi.org/10.1063/5.0173097
5. S.-H. Kwon, J.-H. Kang, C. Seassal, S.-K. Kim, P. Regreny, Y.-H. Lee, C. M. Lieber, H.-G. Park, "Subwavelength Plasmonic Lasing from a Semiconductor Nanodisk with Silver Nanopan Cavity" Nano. Lett., 10(9), (12th August 2010), 2010, https://doi.org/10.1021/nl1021706
6. R.-M. Ma, R. F. Oulton, V. J. Sorger, G. Bartal, X. Zhang, "Room-temperature sub-diffraction-limited plasmon laser by total internal reflection" Nat. Mater., 10(110-113), (19th December 2011), https://doi.org/10.1038/nmat2919
7. F. Montanarella, D. Urbonas, L. Chadwick, P. G. Moerman, P. J. Baesjou, R. F. Mahrt, A. van Blaaderen, T. Stöferle, D. Vanmaekelbergh, "Lasing Supraparticles Self-Assembled from Nanocrystals" ACS. Nano., 12(12), (12th December 2018), https://doi.org/10.1021/acsnano.8b07896
8. P. U. Alves, N. Laurand, M. D. Dawson, "Multicolor laser oscillation in a single self-assembled colloidal quantum dot microsphere" IPC 2020, Proceedings of the 2020 IEEE Photonics Conference, 1-2, (29th September – 1st October 2020); doi: 10.1109/IPC47351.2020.9252438
9. P. U. Alves, D. Jevtics, M. J. Strain, M. D. Dawson, N. Laurand, "Enhancing Self-Assembled Colloidal Quantum Dot Microsphere Lasers" IPC 2021, Proceedings of the 2021 IEEE Photonics Conference (IPC), 1-2, (18th – 21st October 2021); doi: 10.1109/IPC48725.2021.9592976
10. M. I. Stockman, "Brief history of spaser from conception to the future" Adv. Photon. 2(5), (30th October 2020), https://doi.org/10.1117/1.AP.2.5.054002
11. M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalaev, E. E. Narimanov, S. Stout, E. Hertz, T. Suteewong, U. Wiesner, "Demonstration of a spaser-based nanolaser" Nature. 460(1110-1112), (16th August 2009), https://doi.org/10.1038/nature08318
12. Y. Fu, Y. M. Qing, Z. Li, A. V. Zayats, D. Lei, "Tale of Two Resonances: Waveguide–Plasmon Coupling and High Q-Factor Engineering on the Nanoscale" ACS. Photonics. 10(1), (5th December 2022), https://doi.org/10.1021/acsphotonics.2c01271
13. J. A. Jenkins, L. Dube, Y. Luo, J. Chen, T.-H. Fan, Y. Lei, J. Zhao, "A polymer hydrogel modified lateral flow sensing platform" Sensor. Actuat. B. Chem., 262(493-498), (1st June 2018), https://doi.org/10.1016/j.snb.2018.01.214

14. G. Frens, “Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions” Nature., 241(20-22), (1st January 1973), https://doi.org/10.1038/physci241020a0
15. X. Wang, Q. Liao, Q. Kong, Y. Zhang, Z. Xu, X. Lu, H. Fu, “Whispering-Gallery-Mode Microlaser Based on Self-Assembled Organic Single-Crystalline Hexagonal Microdisks” Angew. Chem. Int. Ed., 53(23), (24th April 2014), https://doi.org/10.1002/anie.201310659
16. J. Zhu, S. K. Özdemir, H. Yilmaz, B. Peng, M. Dong, M. Tomes, T. Carmon, L. Yang, “Interfacing whispering-gallery microresonators and free space light with cavity enhanced Rayleigh scattering” Sci. Rep. 4(6396), (17th September 2014), https://doi.org/10.1038/srep06396