Nano-Sized light emitting devices have a wide range of potential applications, from medicine to all-optical computing [1–4]. Surface plasmon amplification by stimulated emission of radiation (SPASER) have recently attracted considerable attention providing the smallest reliable lasers [5, 6]. Plasmonic assisted lasing has been demonstrated in a variety of geometries, embedded in or embedding a gain media. Despite these efforts, the physics underlying a realistic SPASER remains to date only drafted, because of the controversial and the limited number of experimental results. Here we demonstrate unambiguous coherent emission from polyhedral silver nano-particles dispersed in liquid gain media evidenced clearly by the narrowing of the spectral linewidth up to 3-5 nm, the several competing SPASER modes and the nonlinear effects as emission saturation and energy dependent spectral shifts. These novel results open the way to a variety of applications, as the emission of ultrashort optical pulses from nano-size lasers.

Understanding the fundamental light-matter interactions at a scale much smaller than the wavelength is pivotal to any effort to reliably engineer nano-sized laser emission, i.e. controlling their frequency and bandwidth, and ultimately emitting ultrashort laser pulses. The SPASER is a nanometer scale source of intense coherent optical fields with applications ranging from biomedicine to lithography, from microscopy to information technology [1–4, 7]. An optical field around metallic nano-objects surrounded by dielectric media (e. g. air, water, or amorphous materials) can sustain oscillations of free electrons localized at the metal/dielectric interface [8–11]. Electrons are constrained to move as density-waves along the metal/dielectric junction generating localized surface plasmon (SP) oscillations [12, 13]; these are coherent and accumulate energy from the external excitation. Plasmonic stimulated emission of light is obtained when the electronic losses due to absorption are compensated by an optically active medium surrounding the metal nanoparticles [14–16]. Examples of SPASERS have been reported as metal nano-spheres [6, 17, 18] or nano-rods [19] embedded in a gain medium emitting coherent radiation, as semi-conducting waveguides [20, 21] or metamaterials [22, 23]. In most investigated systems the spasing coherent emission has been demonstrated by the strong increase of the emitted radiation intensity, while other paradigms that are used for standard macroscopic lasers such as spectral narrowing through pump threshold, multimodal excitations, gain saturation and non-resonant nonlinearities have been marginally considered and not clearly reported.

Here we show the existence of these effects in a SPASER based on polyhedral silver nanoparticles (nPs), with plasmonic response determined by their shape and polydispersity. Our results remove any doubt about the laser-like behavior of surface plasmonic emission and confirm absolutely that nano scaled metallic particles act as SPASERS. Moreover we demonstrate that SPASER action can be indeed observed in very dilute transparent samples, in contrast with random lasing [24, 25]; the latter relying on the multiple scattering of light involving several particles in a volume, the former being sustained by a single nano-sized particle.

Figure 1a presents a selection of the main samples used in this work; their absorption spectra are shown in Fig.1b. Both Fig.1a and 1b illustrate the tunability of the plasmon resonances of the metal nPs prepared by reduction and photoreduction of silver ions in aqueous media [26, 27]. The different colors correspond to nPs with varied polyhedral morphologies, obtained tuning the synthetic parameters (see Methods). The transmission electron microscopy (TEM) images of two examples are shown in Fig.1c-d, for decahedral and prismatic shapes, respectively. The resonance located around 400 nm is characteristic of spherical silver nPs and presents little variation with the size of the nPs [28], while lower energy resonances are associated with silver nPs of a varied aspect ratios and dimensions. In our experiments the metallic nPs are dispersed in RhodamineB solution (see Methods) acting as gain medium once the system is pumped. The dye emission is depicted in Fig.1b that shows that the plasmonic modes in our samples are excited at in a wavelength range peaked at 590 nm. Fig.2 shows the measured SPASER emission from our samples: by increasing the input pump energy the fluorescence

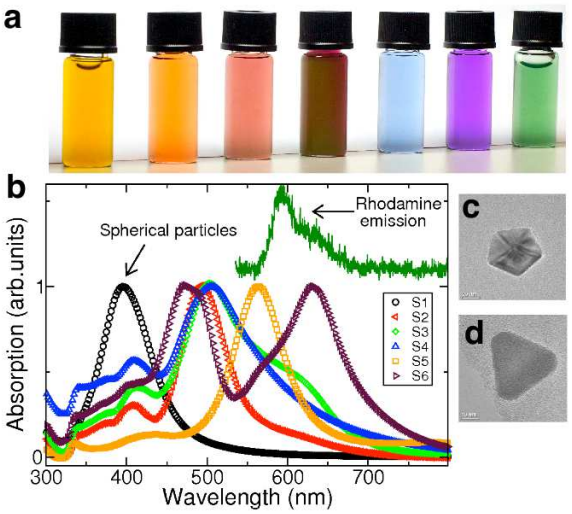

FIG. 1: **Morphology dependent colors.** (**a**) Pictures of selected samples; **(b)** Absorption spectra of various suspensions names S1-S6 and the emission of the adopted pure dye solution; **(c,d)** TEM images of silver nanodecaheadrons and nanoprisms.

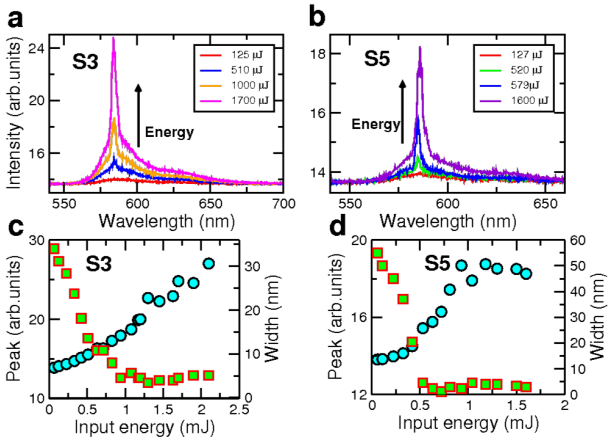

FIG. 2: **SPASER emission.** **(a)** Emission spectra at increasing pump energy of samples S3 and **(b)** S5; the insets show an enlargement of lowest energy spectra. **(c)** spectral width, calculated as half maximum full width (■) and height (●) for sample S3 when increasing input energy; **(d)** as in (c) for sample S5.

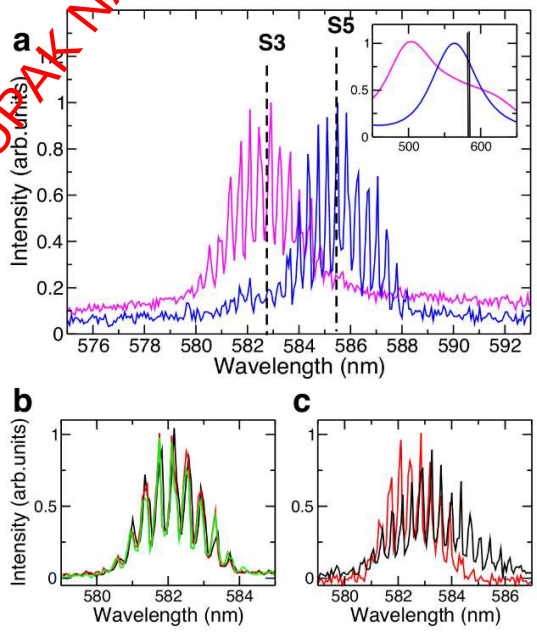

FIG. 3: **Multi-modal SPASER emission.** **(a)** Spectra of samples S3 and S5; the inset shows the corresponding absorption spectra with vertical lines corresponding to the position of SPASER emission; **(b)** Three different spectra from the same sample (S4) taken at time interval of one hour; **(c)** Two different emission spectra from samples S6 (black line) and half-diluted S6 (red line).

spectrum of Rhodamine-B displays a pronounced peak that progressively becomes sharper and more intense, as reported in the panel a and b for samples S3 and S5, respectively. Fig. 2c-d presents the spectral width and peak as a function of the pump energy, unveiling the transition to a coherent emission of the SPASERs, with a line-width of ∼3 nm, lower than those in previously reported investigations [6]. Evidence of the saturation of the emission, corresponding to a trend of the peak intensity deviating from a straight line is shown in Fig.2c. This effect has so far not been reported, and signals the occurrence of a strong nonlinear regime (see below).

The spectral emission could be further investigated by using a higher spectral resolution (0.3 nm), and two representative results are shown in Fig. 3a. Similar multimodal oscillations are observed for all the considered samples presented in Fig. 1a. Two effects are evident: *i*) the peaks of whole spectra have different positions due to differences specific morphology of the nPs in the samples, as these induce different plasmonic oscillations influencing the optical response e.g. the extinction spectra. Noticeably, the spectral positions of the peaks is located between the maximum of the absorption (Fig.1, corresponding for instance to about 500 nm for sample S3 and 550 nm for sample S5), and the peak of the dye emission (corresponding to 590 nm); *ii*) each spectrum displays several spectral resonances that we do not observe in pure dye-water solutions and correspond to various SPASER modes. Such a multi-modal oscillation was not reported before.

The spectral peaks with a spectral period of about 0.5 nm are justified by previous theoretical analyses which predicted that these kind of polyhedral nano-particles sustain various plasmonic oscillations [8]. These modes are known to have a limited coupling with external excitation when measuring absorption, however they are all expected to contribute to laser emission [4]. The observed equispaced resonances are also ascribed to mode

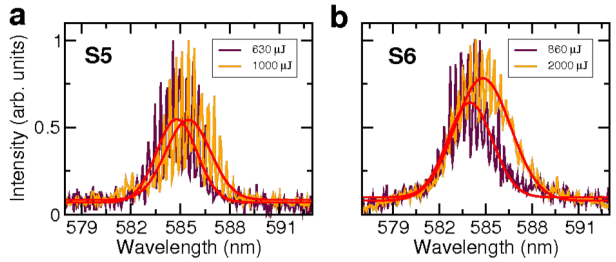

FIG. 4: **Kerr effect in the SPASER emission.** Experimental spectra from S5 **(a)** and S6 **(b)** taken at increased input energy. Solid lines are guides for the eye.

competition and level repulsion [29].

The reproducibility of the oscillations is demonstrated in Fig. 3b with three different spectra from the same sample (S4) taken at time intervals of the order of one hour. We further verified that in the present system the cavity is made by single metal particles by comparing the emission of sample S6 to that of half-diluted concentration (Fig. 3c). The almost perfect overlap shows that the SPASER effect is not related to the amount of nPs. The slight discrepancy is ascribed to some nanoparticle aggregates that may form at higher concentration. This result shows that the emission reported in Fig. 2 is due to SP oscillations and is totally different from random lasers, where the resonator is made of a collection of particles that refract radiation entrapping it [25]. It is also noticeable that optical Kerr effect may occur [30] and be enhanced by the enormous electromagnetic concentration in plasmonic resonances. This may eventually result into an energy dependent spectral shift. Experimental evidences of this phenomenon is shown in Fig. 4a-b for some representative cases, which illustrate how increased input energy induces a red-shift of the emission, up to 7 nm/mJ, and demonstrate the relevance of the non-resonant nonlinearities in the SPASER emission. This explains the gain saturation observed in 2d: as the resonances shift when increasing energy, their position with respect to the maximum gain changes and this negative feedback results into a limited amplification.

In conclusion we have unveiled novel aspects of the rich dynamics of SPASERs, and specifically the pronounced non-linear regimes that can be achieved. Highlighting extremely strong light-matter interactions, these novel features include gain saturation, multi-modal oscillations, and the first evidence of the Kerr effect. These results pave the way to the exploration of novel fundamental physical phenomena relative to nonlinear regimes at a spatial scale much smaller than the wavelength, as well as to innovative applications such as novel kind of laser sources providing ultra-short pulsed operation and structural tunability, realization of ultrafast microprocessors working at THz clock speed, supercontinuum generation, ultrasensing, ultradense and ultrafast information storage.

METHODS

Ag nPs preparation & Characterisation

The silver nPs syntheses were carried out under ambient conditions according to modified protocols reported in the literature. Silver nitrate ($AgNO_3$, 99.0% ACS grade), tri-sodium citrate ($C_6H_5O_7Na_3.2H_2O$, 99% ACS grade), sodium borohydride ($NaBH_4$, 99% ReagentPlus), polyvinylpyrrolidone (PVP, $M_W \sim 55$ kD), L-Arginine ($C_6N_4H_{14}O_2$, 98% reagent grade) were purchased from Sigma-Aldrich and used without further purification. For a typical preparation of spherical silver nPs [27], silver nitrate solution (200 μL, 100 mM) was diluted in DI-water, the citrate solution (160 μL, 400 mM) was then added to act as a stabilizer for the nPs. Under vigorous stirring, a sodium borohydride solution (300 μL, 150 mM) was added drop-wise, initially leading to a black solution quickly turning into a yellow-brown solution. If stirring is stopped before the ageing is completed then part of the nPs falls out of solution. To address this effect and to obtain very stable colloidal solutions, the syntheses were left under stirring to age for at least 24 hrs. The total volume of the nPs solution was set to 20 mL but can easily be scaled up. Photoreduction has become a popular pathway to produce nPs of controlled shape including prism, and decahedral nPs [26]. Starting from small spherical nPs, their growth under varied light exposure conditions allowed the preparation of nPs with tunable decahedron and prism populations. In a typical synthesis, citrate solution (127 μL, 250 mM), PVP (19 μL, 50 mM), L-arginine (16 μL, 20 mM) and silver nitrate solution (25 μL, 50 mM) were successively mixed into DI-water. Sodium borohydride solution (102 μL, 100 mM) was swiftly injected leading a yellow pale solution which was exposed to light sources. The exposure conditions varied from from 24 h to 2 weeks, and from monochromatic to white lights. Extraction by ultra-centrifugation was used to purify the as-prepared nPs solutions. Transmission electron microscopy (TEM) images were recorded using a Gatan CCD camera on a JEOL JEM-2011 electron microscope operating at 200 kV.

Photophysical charactisation

A 0.1 mM Rhodamine B water solution was mixed to the nPs and transfered in 1 mm optical path quartz cuvettes. A Coherent Surelite Q-switched frequency doubled Nd:YAG laser at wavelength λ=532 nm (repetition rate 10 Hz, pulse duration 6 ns and with 8 mm beam waist) was used for optical pumping. For each sample, the laser was focused down to a spot of 1 mm lateral dimension and the emitted radiation was collected from the input face. After focalization into an optic fiber con-

nected to a Horiba MicroHR spectrograph equipped with Symphony electrically cooled CCD array detector. The exposure time was set to 1 s and each spectrum results from the average of 10 pump shots.

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STATEMENT OF AUTHORS CONTRIBUTION

N.G. and C. C. worked on the experimental characterization of the spaser emission. P.A. and A.D.F. worked on the samples preparation and characterization. All the authors equally contributed to interpret the results and to write the manuscript.

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