Research article

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Two-dimensional Au & Ag hybrid plasmonic nanoparticle network: broadband nonlinear optical response and applications for pulsed laser generation

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Abstract: Localized surface plasmon resonance (LSPR) of metallic nanoparticles (NPs) can generate and enhance the nonlinear optical (NLO) response and has been widely used in biosensing, optical bistability, optical switch, and modulator, surface-enhanced spectroscopies, etc. Here, the two-dimensional (2D) Au & Ag hybrid plasmonic NP network (Au & Ag HPNN) were synthesized by assembling Au and Ag NPs in ethanol solvent and transferring onto a CaF₂ substrate. The frequency-domain finite element method (FEM) simulations were performed to explore their LSPR properties, demonstrating the broadband optical responses throughout visible, near-infrared and mid-infrared regions. The ultrafast carrier relaxation times were determined to be 3.9, 5.6, and 8.6 ps, while the nonlinear absorption coefficients were -1.12×10^4 , -1.71×10^4 , and -2.54×10^4 cm/GW, respectively, for the three wavelengths matching the LSPRs peaks at 1.0, 2.0, and 3.0 μ m bands. Furthermore, passively Q-switched (PQS) solid-state lasers operating at 1062.8, 1990.8, and 2947 nm were demonstrated with 2D Au & Ag HPNN based saturable absorbers. This work not only reveals desirable ultrafast broadband NLO responses of 2D HPNN, but also provides a

platform for investigating their applications in nanophotonic devices.

Keywords: broadband nonlinear optical response; localized surface plasmon resonance; passively Q-switched solid-state lasers.

1 Introduction

Nonlinear optical (NLO) response plays a significant role in modern nanophotonics, which generates a great deal of interests in the design, preparation, and characterizations of new NLO nanomaterials. Recently, there has been an increasing interests in NLO properties of metallic nanoparticles (NPs), which have proved to be highly valuable for a variety of applications including plasmon-enhanced spectroscopies, biosensing, optical tweezers, optical bistability, ultrafast optical switch and modulation, optoelectronic devices, and so on [1–7]. The NLO responses of metallic NPs are in a large extent determined by the plasmonic resonances (surface plasmon resonance (SPR) for extended metallic surfaces, and localized surface plasmon resonance (LSPR) for metallic NPs), which are the conduction electron coherent oscillations stimulated by the incident light and strongly dependent on NPs' geometry and surroundings [1, 8–13]. Therefore, it provides a great platform for modulating the optical responses by tuning the metallic NPs' shapes, sizes, and environments, etc.

Up to now, various types (e. g., materials, shapes, sizes, surroundings, etc.) of plasmonic NPs have been designed and fabricated for specific scientific researches and applications [6, 14–20]. In particular, the excellent third-order NLO properties in terms of a large third-order nonlinear susceptibility, an ultrafast relaxation time, the suitable modulation depth, and saturation intensity, make metallic NPs to be an excellent saturable absorber (SA), which is the

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key element of the passively Q-switched (PQS) or mode-locked pulsed lasers [21–25]. In noble metal NPs, Au and Ag are the two most frequently and widely studied plasmonic materials due to the advantages including but are not limited to the following: First, easy fabrication makes it possible to synthesize Au NPs and Ag NPs with different shapes, sizes, as well as external factors, leading to the ability of manipulating the plasmonic functionalities and applications [26, 27]; Second, the LSPR of Au NPs and Ag NPs can be tuned throughout the visible, infrared and even mid-infrared (MIR) regions [21, 28]; Third, they have large nonlinear saturable absorption coefficient and third-order nonlinear susceptibilities, which are comparable to that of the novel two-dimensional (2D) materials [29, 30]; Fourth, the ultrafast response on the time scale of femtoseconds or picoseconds makes Au NPs and Ag NPs to exhibit great potential in ultrafast optical signal processing [21, 31]. What's more, LSPRs of NPs can be effectively enhanced by coupling plasmonic NPs to form the nanostructures such as chains, dimers, trimers, and even 2D networks/clusters. The distance and width of sintering parts between plasmonic NPs turn out to be extremely important for determining LSPRs coupling and therefore the resulting spectrum and electric field enhancement [11, 12]. Au NPs and Ag NPs can be easily assembled to form plasmonic nanostructures like one-dimensional (1D) chains and 2D networks/clusters, which can consequently offer a unique strategy for tuning the LSPRs of the plasmonic nanostructures [32].

The plasmonic-driven NLO properties and applications of single component Au NPs or Ag NPs as well as the alloyed or bimetallic Au–Ag NPs have been widely studied [23]. However, the third-order NLO properties of hybrid structures of Au NPs and Ag NPs have been rarely investigated. Novel NLO responses can be presented when mixing Au NPs and Ag NPs together to form the hybrid 1D chains or 2D network due to the coupling of the plasmonic effects like alloy or bimetallic nanostructures, which has proved to exhibit much better and larger tunability of NLO properties than that of mono-element NPs [23]. For alloy or bimetallic nanostructures, some typical vibrational peaks would attenuate while several novel resonance peaks can be generated and enhanced, such as capacitive chain plasmon (CCP) resonance peaks, and threaded chain plasmon (TCP) resonance peaks, which are caused by the charge conduction on neighboring NPs or entire chain [11, 12]. Furthermore, modifying the number and the dimensions of AuNPs and Ag NPs can effectively tune the LSPRs. For example, by extending the length of the chain and increasing the NPs' size, the plasmonic peak position will be red-shifted, meanwhile, the corresponding full width at half maximum (FWHM) will be broadened [33, 34].

In this paper, Au & Ag hybrid plasmonic nanoparticle networks (Au & Ag HPNN) were designed and successfully fabricated by assembling Au NPs and Ag NPs in ethanol solvent and transferring them onto a CaF_2 substrate. The LSPR properties of the 2D Au & Ag HPNN in terms of the extinction spectrum, field amplitude and phase distributions were calculated by frequency-domain finite element method (FEM). Open-aperture Z-scan and non-degenerate ultrafast pump-probe techniques were performed to explore their broadband saturable absorption and ultrafast relaxation dynamic properties at the three wavelengths matching the LSPR peaks at 1.0, 2.0, and 3.0 μm . Moreover, the PQS solid-state lasers operating at 1062.8, 1990.8, and 2947 nm were achieved by using the as-prepared 2D Au & Ag HPNN as the SAs. The results demonstrated that the Au & Ag HPNN SA can support pulse modulation in the near-infrared to mid-infrared band in solid state lasers.

2 Results and discussion

2.1 Preparation and characterization of hybrid isolated 2D Au & Ag HPNN

Recently, the hybrid plasmonic nanostructures with the core of a plasmonic NP covered by another thin shell have been widely studied. But the synthesization process is still challenging because of the requisite use of templates, ligands, polymers, molecular linkers, and intricate post-assembly separation process, which make it hardly to reproduce and scale up. Herein, we designed the 2D Au & Ag HPNN by assembling Au NPs and Ag NPs in ethanol solvent. The synthesization process is shown in Figure 1a. The individual Au NPs with diameters of ~ 16 and Ag NPs with diameters of ~ 23 nm were firstly synthesized, which is described in the experimental section. The transmission electron microscopy (TEM) and histograms of the monodisperse particle sizes of Au NPs and Ag NPs shown in Figure S1 are made up of 16 ± 0.5 nm Au NPs and 23 ± 2 nm Ag NPs. The corresponding particle concentrations of Au NPs and Ag NPs were calculated to be 1.15×10^{12} and $4.75 \times 10^{11}/\text{mL}$, respectively. Then, the solutions of as-prepared Au NPs and Ag NPs were mixed in the ethanol solvent, in which the approximated number ratio of Au NPs and Ag NPs is 7:6. After mixing in the ethanol solvent, the Au NPs and Ag NPs became unstable and began to assemble. Once some two NPs coupled to form a dimer driven primarily by dipolar interactions and van der Waals forces, other neighboring NPs were preferentially attached to the ends of the dimer rather than to the sides because of the anisotropic character of the electrostatic repulsion between the surrounding NPs, thus leading to form the linear

Figure 1: (a) Fabrication process of 2D Au & Ag HPNN; (b) and (c) HAADF-STEM-EDS Mapping of assembled Au NPs (red) and Ag NPs (green); (d) TEM images and HR-TEM image of Au & Ag NPs and part of 1D Au & Ag NPs chain.

hybrid NPs trimers, tetramers, 1D chains, and eventually 2D nanoparticle network [35]. The extinction spectra of the mixing solution of Au NPs and Ag NPs obtained at different standing time shown in Figure S2(a) verifies the formation of short chains made up of Au NPs and Ag NPs. Figure S2b and c shows the extinction spectra of as-synthesized Au and Ag NPs separately [36, 37]. After 3 h standing, Au & Ag HPNN formed in the ethanol solution were then transferred onto a CaF₂ substrate by spin-coating method.

Figure 1b and c shows the typical TEM images of 2D Au & Ag HPNN. The width of sintering parts between the neighboring NPs was measured to be ~ 0.71 nm (shown in inset of Figure 1d). Figure 1c shows the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersion X-ray spectroscopy (EDS) mapping of 2D Au & Ag HPNN, which further confirms the formation of hybrid nanostructure. Figure 1d shows the high-resolution electron transmission microscopy (HR-TEM) image of the prepared Au & Ag NPs and part of 1D Au & Ag NPs chain. The

TEM of several different positions and scanning electron microscopy (SEM) images on the substrate are shown in Figure S3 and Figure S4, giving clear evidence about the presence of sintering parts between Au NPs and Ag NPs. Moreover, it can also be found that the particle ratio between Au NPs and Ag NPs is around $\sim 7:6$ on the basis of statistic result from the TEM images, which is consistent with that used in the fabrication process. Furthermore, the NP number in the typical 1D chain is $N = \sim 13$, and the typical Au NPs and Ag NPs distributions are in the orders like “Ag-Au-Ag-Au-Ag-Ag-Au-Ag-Au-Au-Au-Ag-Au-Ag-Au”.

2.2 Theoretical simulations of the tunable LSPRs

It has proved that the local 1D chain plasmonic modes can be used to explain most of the observed NLO responses of the 2D or three dimensional (3D) networks, aggregates, or

clusters. The field and spectrum enhancement of the 2D or 3D clusters are generally consistent with the interpretation of optical response in terms of local 1D chain modes [38]. The frequency-domain FEM were performed to investigate the optical response (LSPRs) of the prepared 2D Au & Ag HPNN in terms of extinction spectrums, normalized electric field amplitude and phase distributions. We first calculated the contributions of 1D chain with the different numbers of nanoparticles to the optical response as shown in Figure S5 and then extend it to the 2D network/aggregates form. Figure 2a shows the calculated extinction, scattering, and absorption spectrums of the 2D Au & Ag HPNN (corresponding to LSPRs peaks), while Figure 2b exhibits the corresponding normalized electric field amplitude (left contours) and the phase (right contours) distributions. There exist four main absorption peaks centered at 400, 1250, 1500, and 2700 nm, corresponding to CCP, CTP1, CTP2, and CTP3 (1, 2, and 3 corresponding to the first, second and third-order of CTP modes) resonance modes. For the two different modes, the CCP mode is associated with a collective plasmon excitation of the nanoparticles forming the chain, which behaves like a long electric dipole. The CTP mode is associated with charge transfer along the entire nanoparticle string. From Figure 2a, it can be observed that the scattering cross-section is much lower than that of the absorption, which indicates the 2D Au & Ag HPNN should have excellent optical absorption properties. The simulation results show that by mixing Au NPs and Ag NPs together to form the 2D Au & Ag HPNN can tune and extend the corresponding optical response to the MIR region.

2.3 Ultrafast dynamic and NLO absorption properties

For noble metallic nanoparticles, the plasmonic effects are the key features dominating their NLO responses, which are governed by two fundamental processes: photoexcitation and ultrafast carrier relaxation. The latter can respond on the timescale of a few femtoseconds or picoseconds, which can allow ultrafast processing of optical signals. A non-degenerate femtosecond ultrafast pump-probe technique with a pump laser operating at 800 nm and three probe lasers operating at 1.0, 2.0, and 3.0 μm (matching the calculated LSPRs peaks), was used to explore the carrier dynamics of the as-prepared 2D Au & Ag HPNN. The measurement setup is shown in Figure S6, and the details are described in the experimental section. During the pump-probe measurement, the pump beam excites the electrons of Au NPs and Ag NPs from occupied to unoccupied states by intra-band absorption processes (the free-electron relaxation time induced by LSPR), while the probe beam monitors the pump induced transmission variation ($\Delta T/T_0$) as a function of the pump-probe laser beam time delay. Here, T_0 is the probe laser transmission before the pump laser excitation, and ΔT is the corresponding probe laser transmission variation after the pump laser excitation. Figure 3a–c shows the transient optical responses of the 2D Au & Ag HPNN at three probe wavelengths of 1.0, 2.0, and 3.0 μm , respectively. The observed positive $\Delta T/T_0$ signals reveal the photobleaching features caused by the Pauli blocking effect, which

Figure 2: (a) Extinction, absorption and scattering cross section of the hybrid isolated 2D Au & Ag HPNN. (b) The corresponding electric field amplitude (left contours) and phase distribution (right contours).

Figure 3: (a)–(c) Ultrafast transient optical responses of the 2D Au & Ag HPNN with the probe laser operating at 1.0 (a), 2.0 (b), and 3.0 μm (c); (d)–(f) The typical open-aperture Z-scan curves at the three wavelengths of 1064 (d), 1990 (e), and 2950 μm (f).

indicates that the 2D Au & Ag HPNN exhibits a broadband saturable absorption effect in the wavelength band of 1.0, 2.0, and 3.0 μm . As for reference, a pure CaF_2 substrate was measured under the same condition. No transient response was detected, indicating the dynamic response was only attributed by Au NPs and Ag NPs.

For non-degenerate pump-probe measurements, the measured $\Delta T/T_0$ delay can be fitted by the exponential decay function [39]:

$$\frac{\Delta T}{T_0} = A_1 + A_2 \exp(-t/\tau) \quad (1)$$

where A_1 and A_2 are the relative amplitudes of the double temporal components, τ is the relaxation time determined by electron–electron (hot-electron thermalization). The

carrier-carrier scattering time is very short with a time regime of ~ 10 – 200 fs, which is hardly to detect under the resolution of our experimental setup (~ 170 fs ($\Delta t_{\min} = \Delta d/2c$, $\Delta d = \sim 0.1$ mm)). Therefore, the relaxation process is generally fitted by using Equation (1), τ was fitted and calculated to be 3.9, 5.6, and 8.6 ps respectively for 1.0, 2.0, and 3.0 μm . It is on the same time scale as Au (~ 2 ps) and Ag (~ 0.7 ps) mono-element nanoparticles [40, 41]. The ultrafast relaxation time is benefited for ultrafast optical signals processing.

For plasmonic Au NPs or Ag NPs, the LSPR is prominent in NLO responses at the resonance wavelengths. As well known, it decays through both radiative and non-radiative processes by three different routes, namely, radiative scattering or emission, non-radiative inter-band, and intra-band absorption. Since the luminescence

Table 1: Ultrafast dynamic and NLO properties parameters of several typical noble material.

Materials	Laser parameters	Relaxation time (ps)	β_{eff} (cm/GW)	$\text{Im}(\chi^{(3)})$ (esu)	Ref.
Ag ¹	He-Ne laser at 632.8 nm	—	1.5×10^6	1.47×10^{-4}	[43]
Au:Al ₂ O ₃ ²	7 ns 532 nm 10 Hz	—	-1.31×10^6	-5.33×10^{-7}	[29]
Au:SiO ₂ ²	7 ns 532 nm 10 Hz	—	-0.12×10^6	-0.067×10^{-7}	[29]
Au:ZnO ²	7 ns 532 nm 10 Hz	—	-0.08×10^6	-0.044×10^{-7}	[29]
Au:H ₂ O ³	30 ps 532 nm 10 Hz	~29	—	$2-4 \times 10^{-8}$	[44]
Au-Ag ⁴	6 ps 527 nm 1 Hz	—	-3.42×10^5	—	[45]
Au:αAl ₂ O ₃ ⁵	26 ps 532 nm 1–10 Hz	30	-2.37×10^4	—	[46]
Ag ⁶	26 ps 355 nm 10 Hz	—	–2.15	—	[47]
Ag ⁶	26 ps 532 nm 10 Hz	—	–0.25	—	[47]
Ag ⁶	26 ps 1064 nm 10 Hz	—	–0.229	—	[47]
Au ⁷	50 fs 800 nm 1 kHz	—	–13	—	[48]
Au ⁸	17 ns 308 nm 2 Hz	—	—	-1×10^{-9}	[49]
Au nanorods ⁹	90 fs 796 nm 1 kHz	5.7	–0.307	-8.7×10^{-14}	[50]
Au nanostars ⁹	90 fs 796 nm 1 kHz	3.1	–0.14	-4×10^{-14}	[50]
Au nanoshells ⁹	90 fs 796 nm 1 kHz	1.8	0.016	-0.45×10^{-14}	[50]
Au:Al ₂ O ₃ ¹⁰	150 fs 780 nm 1 kHz	1.42	—	—	[51]
Ag-coated GNRs ¹¹	130 fs 750 nm 76 MHz	0.93–1.7	—	3.35×10^{-11}	[52]
Au nanorods ¹¹	130 fs 750 nm 76 MHz	—	—	-2.58×10^{-11}	[52]
Au _{0.5} Ag _{0.5} ¹²	35 ps 532 nm 1–10 Hz	—	-2.8×10^{-4}	-1.3×10^{-15}	[53]
Au ¹²	35 ps 532 nm 1–10 Hz	—	-4.96×10^{-3}	-2.28×10^{-14}	[53]
Ag ¹²	35 ps 532 nm 1–10 Hz	—	-4×10^{-5}	-2×10^{-16}	[53]
2D Au & Ag HPNN	25 ns 1064 nm 50 kHz	3.9	-1.12×10^4	-8.23×10^{-9}	This work
	25 ns 1064 nm 50 kHz	5.6	-1.71×10^4	-2.04×10^{-8}	
	25 ns 1064 nm 50 kHz	8.6	-2.54×10^4	-5.28×10^{-8}	

efficiency of Au NPs and Ag NPs is relatively low (according to scattering of the FEM simulation), LSPR decay occurs mainly through the non-radiative inter- and intra-band absorption processes, resulting in free carriers (hot-electrons) generation. Here, the open-aperture Z-scan method was applied to explore the third-order NLO responses of the prepared 2D Au & Ag HPNN by measuring the intensity-dependent normalized transmittances of the sample. The experimental setup is shown in Figure S7a. The details are described in the experimental section. Figure 3d–f shows the Z-scan curves at three wavelengths of 1064, 1990, and 2950 nm. The peak-like curve symmetric to the focus point ($z = 0$) can be observed for the three wavelengths, i. e., the transmittance increases with increasing the incident laser intensity, which is a typical evident for saturable absorption response. Based on the NLO theory, the nonlinear absorption coefficient β_{eff} and the imaginary part of the third-order susceptibility $\text{Im}(\chi^{(3)})$ can be obtained by fitting the Z-scan curve (the fitting and calculation processes are described in supporting information). β_{eff} and $\text{Im}(\chi^{(3)})$ were determined to be -1.12×10^4 , -1.71×10^4 , -2.54×10^4 cm/GW and -8.23×10^{-9} , -2.04×10^{-8} , -5.28×10^{-8} esu for 1064, 1990, and 2950 nm, respectively. The negative nonlinear absorption coefficient β_{eff} further confirms the saturable absorption characters of the prepared 2D Au & Ag HPNN.

Table 1 summarizes β_{eff} and $\text{Im}(\chi^{(3)})$ of different Au and Ag plasmonic nanostructures. The β_{eff} and $\text{Im}(\chi^{(3)})$ values of 2D Au & Ag HPNN in our experiment are a little bit larger than that of the mono-element Au and Ag nanostructures, which may be due to the different pulse widths of the measurement light source [42].

To get the saturable absorption parameters of the prepared 2D Au & Ag HPNN, Z-scan curves were depicted and fitted by the following formula [54]:

$$T_n = \left(1 - \frac{\Delta R \times I_s}{I_s + I_0 / (1 + Z^2 / Z_0^2)} \right) / (1 - \Delta R) \quad (2)$$

where T_n is the nonlinear transmittance, ΔR is the modulation depth, I_s is the saturation fluence, I_0 is the incident intensity, Z and Z_0 are the relative position of the sample and diffraction length of the light, respectively. By fitting the curve, the modulation depth, and the saturation fluence were determined to be 14%, 12.4 $\mu\text{J}/\text{cm}^2$ for 1064 nm; 11.2%, 6.6 $\mu\text{J}/\text{cm}^2$ for 1990 nm; and 9.1%, 3.4 $\mu\text{J}/\text{cm}^2$ for 2950 nm, respectively. The nonlinear transmission curves as a function of the incident energy intensity were also measured by the balanced dual-detector method. The results are shown in Figure S7b–d, which further illustrate the saturable absorption properties of the prepared 2D Au & Ag HPNN at the three wavelengths.

Figure 4: (a)–(c) CW and PQS average output powers as the function of the absorbed pump power at 1.0 (a), 2.0 (b), and 3.0 μm (c); (d)–(f) Pulse width and pulse repetition rate versus the absorbed pump power at 1.0 (d), 2.0 (e), and 3.0 μm (f); (g)–(i) The relationship between the single pulse energy, pulse peak power and the absorbed pump power at 1.0 (g), 2.0 (h), and 3.0 μm (i).

2.4 PQS pulsed lasers based on the 2D Au & Ag HPNN

Both pump-probe and open-aperture Z-scan measurements illustrate that the prepared hybrid isolated 2D Au & Ag HPNN have excellent broadband nonlinear saturable absorption properties. In order to further explore their saturable absorption applications, the prepared 2D Au & Ag HPNN (on CaF₂ substrate) were inserted into a simple two-mirror linear laser cavity to act as the SA for generating PQS laser pulses. The experimental setup is shown in Figure S8. The broadband PQS solid-state bulk lasers with three different gain crystals operating at 1064, 1990, and 2950 nm were designed. Based on the second threshold condition, the criterion of a PQS laser can be simplified and described as [55]:

$$\frac{F_{sat,A}}{\Delta R \tau} \leq \frac{2hc\omega_{eff,L}^2}{m\lambda\sigma_{em,L}\omega_{eff,A}^2 T_R} \quad (3)$$

where $F_{sat,A}$ is the saturable energy fluence, ΔR is the modulation depth, τ is the recovery time of the SA, h is the Planck constant, c is the light velocity, λ is the laser wavelength, $\omega_{eff,A}$ and $\omega_{eff,L}$ are the effective laser radii at the position of SA and laser crystal, $\sigma_{em,L}$ is the stimulated emission cross-section of the laser crystal, T_R is the laser cavity round-trip time, and m is a cavity constant, where for linear cavity $m = 2$ and for ring cavity $m = 1$. Considering the characters of three gain crystals, the cavity parameters, and the saturable absorption parameters of the 2D Au & Ag HPNN SAs, the left side of Equation (3) were calculated to be much smaller than the right side (details in supporting information) for the three lasers, which verified the

Figure 5: (a)–(c) Laser output spectrum for both CW and PQS operations at 1.0 (a), 2.0 (b), and 3.0 μm (c); (d)–(f) The typical pulse profiles of the shortest pulse width and pulse trains at the highest pulse repetition rate, respective for 1.0 (d), 2.0 (e), and 3.0 μm (f).

Table 2: Results of the passively Q-switched lasers based on 2D Au & Ag HPNN SA.

Parameters	Nd:YVO ₄	Tm:YAP	Ho,Pr:LLF
Output power (mW)	248	238	157
Pulse width (ns)	574	375	312.9
Repetition rate (kHz)	75	56.06	101
Pulse energy (μJ)	3.31	4.25	1.55
Peak power (W)	5.76	11.32	4.96
Wavelength (nm)	1062.8	1990.8	2947

prepared 2D Au & Ag HPNN SAs were suitable for PQS laser generation with the as-designed laser resonator.

By inserting the 2D Au & Ag HPNN based SA into the laser cavity, the stable PQS laser operation could be obtained by adjusting the resonator elements. Figure 4a–c shows the CW and PQS average output power as a function of the absorbed pump power, from which the conversion efficiency from CW to PQS operations are determined to be 17.1, 54.7, and 46.4% respectively for 1.06, 1.99, and 2.95 μm lasers. Figure 5a–c shows the CW and PQS laser emission spectrum of the three

lasers. The emission wavelengths were all clearly blue-shifted from CW to Q-switching operation, which might due to the insertion losses introduced by 2D Au & Ag HPNN SAs.

The pulse width and repetition rate versus the absorbed pump power are shown in Figure 5d–f. The pulse width decreased, while the repetition rate increased as increasing the pump power. The shortest pulse widths for the three wavelengths were determined to be 574, 375, and 312.9 ns for 1.06, 1.99, and 2.95 μm, corresponding to the largest repetition rate of 75, 56.06, and 101 kHz, respectively. The pulse width is different at three wavelengths, the reason is that for PQS lasers, the pulse width is mainly determined by the characteristics of the crystals (e. g., the upper level lifetime, the stimulated emission section, etc.) and the SA (e. g., modulation depth, initial transmission, saturation intensity, non-saturable loss, etc.), as well as the laser cavity parameters (e. g., the pump level, the transmission of the output coupler, etc.). Considering the different crystal characters, the different Au & Ag HPNN as SA parameters at the three wavelengths, as well as the

different cavity parameters, the pulse width at the three wavelengths are exactly different. The typical pulse profile of the shortest pulse width and the corresponding pulse train of the largest repetition rate are shown in Figure 5d–f. The pulse-to-pulse amplitude instability were recorded and calculated to be less than 4.5% in 1 h operation for the three PQS lasers. Figure 4g–i shows the relationships between the single pulse energy, pulse peak power and the absorbed pump power. The maximum pulse energies were determined to be 3.31, 4.25, and 1.55 μJ respectively for 1.06, 1.99, and 2.95 μm , while the highest peak powers were 5.76, 11.32, and 4.96 W. The detailed output parameters of the three PQS lasers are summarized in Table 2. Compared with the single Au NPs and Ag NPs-based SA, the pulsed width is significantly shorter than previous reports [56–59].

3 Conclusions

In summary, Au NPs and Ag NPs were mixed together to form the novel self-assembled hybrid isolated 2D Au & Ag HPNN. FEM theoretical simulations were performed to study the tunable LSPRs in terms of excitation spectrum, electric field amplitude and phase distributions. The results testified their optical responses can be throughout the visible, near-infrared, and MIR regions. The ultrafast carrier dynamics and nonlinear optical responses were measured by non-degenerate pump-probe and open aperture Z-scan methods. The ultrafast relaxation times were determined to be 3.9, 5.6, and 8.6 ps for 1.0, 2.0, and 3.0 μm . The nonlinear absorption coefficients were measured to be -1.12×10^4 , -1.71×10^4 , and -2.54×10^4 cm/GW respectively at the wavelengths of 1.0, 2.0, and 3.0 μm , which indicate the prepared 2D Au & Ag HPNN have excellent broadband NLO properties. In addition, 2D Au & Ag HPNN based PQS lasers operating at 1.06, 1.99, and 2.95 μm were successfully demonstrated. This work provides an intuitive understanding of NLO properties of 2D Au & Ag HPNN and verifies Au & Ag HPNN or other types of complex network or clusters are promising candidates for ultrafast optical processes, e. g., optical modulation, switchers, biosensors, and so on.

4 Experimental section

4.1 Preparation of 2D Au & Ag HPNN

Aqueous dispersions of citrate-stabilized Au NPs with sizes of ~ 16 nm were firstly synthesized. An aqueous of HAuCl_4 solution (0.50 mL, 25 mM) was added into 48 mL of boiling water without noticeable bubbling under stirring, followed

by further boiling for 10 min. Subsequently, 1.5 mL of aqueous solution of sodium citrate (1 wt%) was rapidly injected into the boiling HAuCl_4 solution under vigorous stirring. The reaction solution was further refluxed for 30 min under stirring to warrant the formation of monodisperse, quasi-spherical Au NPs with sizes of 16 nm. It was assuming that all added Au^{3+} ions were reduced to Au^0 atoms by citrate in solution and formed spherical Au NPs. The particle number concentration can be calculated by $6 m_{\text{Au}} / (\rho_{\text{Au}} \pi d^3 V)$, where m_{Au} is the mass of Au (which is derived from the amount of HAuCl_4), ρ_{Au} is the density of Au, d is the diameter of the corresponding Au NPs, and V is the volume of the solution (in this case, the volume of the solution is 50 mL). Accordingly, the particle number concentrations of 16 nm Au NPs were determined to be $1.15 \times 10^{12}/\text{mL}$.

Ag NPs with diameter of ~ 23 nm were prepared via the ascorbic acid (AA)/citrate reduction protocol 50 μL of aqueous solution of AA (0.10 M) was added to 47.5 mL of boiling water, followed by further boiling for 1 min. One milliliter of aqueous solution of sodium citrate (1 wt%), 0.25 mL of aqueous solution of AgNO_3 (1 wt%), and 200 μL of aqueous solution of NaCl (20 mM) were consecutively added to water with stirring at room temperature. After 5 min of incubation at room temperature, the solutions were injected into the aforementioned boiling aqueous solutions of AA. The color of the reaction solutions quickly changed from colorless to yellow. The transparent and yellow reaction solutions were boiled for another hour with stirring to warrant the formation of uniform, quasi-spherical Ag NPs in the experiments. Similarly, the particle number concentrations of 23 nm Ag NPs were determined to be $4.75 \times 10^{11}/\text{mL}$.

The aqueous dispersions of 1 mL Au NPs and 2 mL Ag NPs were subjected to centrifugation (8000 rpm for 10 min, two times) to remove excess reagents, respectively. Subsequently, the resulting Au NPs and Ag NPs were assembled in ethanol solvent (the particle number ratio of Au NPs and Ag NPs was 7:6). On account of the removal of the stabilizer, the Au NPs and Ag NPs were unstable and begin to aggregate.

Spin-coating process was performed by using a WS-650SZ-6NPP/LITE spinner. Hundred microliters of ethanol solution containing Au & Ag HPNN were firstly casted on a CaF_2 substrate. After the substrate was completely covered by the corresponding liquid, the rotation got started at a set rotation speed of 4000 rpm and duration time of 45 s, respectively.

4.2 FEM simulations

The LSPR properties in terms of extinction spectra, electric field and phase distributions were calculated by electrodynamic simulations using frequency-domain FEM in

COMSOL Multiphysics software package (installed on a Quad Intel Xeon CPU, 128 GB RAM workstation). In the process of simulation, the plane wave illumination was incident from the upward side, normal to the cross profile of NPs chain, with a polarization along the long axis of chain. The dielectric constant of surrounding air was 1, while the dielectric functions $\varepsilon(w)$ of metal of NPs were modeled by a Lorentz–Drude dispersion model fitting the experimental data in Palik’s book [60]:

$$\varepsilon(w) = 1 - \frac{f_0 w_p^2}{w(w - i\Gamma_0)} + \sum_{j=1}^m \frac{f_j w_p^2}{(w_j^2 - w^2) + iw\Gamma_j'} \quad (4)$$

where w_p is the plasma frequency with oscillator strength f_0 and damping constant Γ_0 . The scattering spectroscopy was obtained by integrating the normal Poynting power flow of the scattering wave over the spherical surface enclosing the NPs chain, the absorption was obtained by integrating the electromagnetic dissipation power over all the NPs, and the extinction spectrum was the sum of these two. As well known, FEM was very computational expensive. The computational time for an entire spectrum in this paper, e. g., 95 spectral points in the wavelength range of 300–5000 nm with 50 nm wavelength spacing was around 18 h. The highest spatial resolution of the grid was 0.5 nm at the gaps in all our simulations, which can ensure the numerical accuracy to some extent.

4.3 Non-degenerate ultrafast pump-probe measurement

The ultrafast carrier dynamics of the prepared 2D Au & Ag HPNN were measured by the non-degenerate pump-probe technique. The experimental setup is shown in Figure S6. An 800 nm Ti:sapphire laser system with ultrashort pulse of 100 fs and a repetition rate of 1 kHz was employed. The output beam is split into two parts: one part is used to excite the sample; another one is used to pump an OPA system to generate a probe laser with wavelength tunable from 1.0 to 3.0 μm . The pump and probe laser were focused onto the same position on the sample, where the pump light spot is about 10 times as large as that of the probe laser. A PbSe detector (PDA20H, Thorlabs) with a lock-in amplifier (with a 500 Hz chopped pump) were used for detecting the time-dependent normalized transmission variation of the probe laser introduced by the pump laser.

4.4 Open-aperture Z-scan measurement

The laser source is a widely tunable nanosecond optical parametric oscillator with a tunable range from 1.5 to

3.0 μm and a repetition rate of 50 kHz. The output beam is divided into two beams through a 1:1 beam splitter, one for the calibration light and the other for the probe light. A focusing lens with focus length of 60 cm is used to focus the probe laser beam. The calibration and incident laser intensity were recorded by the power meter (Thorlabs S470C).

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