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Efficient reverse saturable absorption of sol-gel hybrid plasmonic glasses

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ABSTRACT

Monolithic silica sol-gel glasses doped with platinum(II) acetylide complexes possessing respectively four or six phenylacetylene units (PE2-CH_2OH and PE3-CH_2OH) in combination with various concentrations of spherical and bipyramidal gold nanoparticles (AuNPs) known to enhance non-linear optical absorption, were prepared and polished to high optical quality. The non-linear absorption of the glasses was measured and compared to glasses doped solely with AuNPs, a platinum(II) acetylide with shorter delocalized structure, or combinations of both. At 532 nm excitation wavelength the chromophore inhibited the non-linear scattering previously found for glasses only doped with AuNPs. The measured non-linear absorption was attributed to reverse saturable absorption from the chromophore, as previously reported for PE2-CH_2OH/AuNP glasses. At 600 nm strong nonlinear absorption was observed for the PE3-CH_2OH/AuNPs glasses, also attributed to reverse saturable absorption. But contrary to previous findings for PE2-CH_2OH/AuNPs, no distinct enhancement of the non-linear absorption for PE3-CH_2OH/AuNPs was observed. A numerical population model for PE3-CH_2OH was used to give a qualitative explanation of this difference. A stronger linear absorption in PE3-CH_2OH would cause the highly absorbing triplet state to populate quicker during the leading edge of the laser pulse and this would in turn reduce the influence from two-photon absorption enhancement from AuNPs.

1. Introduction

Sol-gel hybrid glasses doped with high concentrations of platinum(II) acetylide based chromophores, named PE2-CH_2OH (Fig. 1) and PE3-CH_2OH (Fig. 2) possessing respectively four or six phenylacetylene units, can be prepared with good optical quality using low temperature sol-gel routes. Such hybrid glasses have previously shown strong and nonlinear broadband absorption (NLA) [1]. The nonlinear optical mechanism is wavelength dependent; singlet ground state one photon absorption with fast intersystem crossing (ISC) to the triplet state dominates < 500 nm, direct ground state singlet to triplet absorption in the range ~500–570 nm, and two-photon absorption (2PA) with fast ISC to the triplet state in the range ~540–700 nm [2–4]. Even though solid state glass materials can now be easily prepared for e.g. optical power limiting (OPL) applications, there is still a need for further improvement and increased doping concentration does not enhance the performance of the glass materials as can be expected [1].

Gold nanoparticles (AuNPs) have been shown to demonstrate enhancement of optical effects in a variety of applications [5–11]. Our investigation of the use of AuNPs for optical enhancement applications started with the preparation of Methyltriethoxysilane (MTEOS) based glasses doped with varying geometries and concentrations of AuNPs [12]. Both spherical (23 or 45 nm diameter) or bipyramidal (largest surface plasmon resonance at 633, 684 or 762 nm) AuNPs were used [12]. At the 532 nm excitation wavelength the glasses showed large non-linear scattering. At 600 nm no or negligible non-linear scattering was found at the input fluences investigated (<5 J/cm^2) [12].

Continuing by co-doping PE2-CH_2OH (Fig. 1) with different sizes

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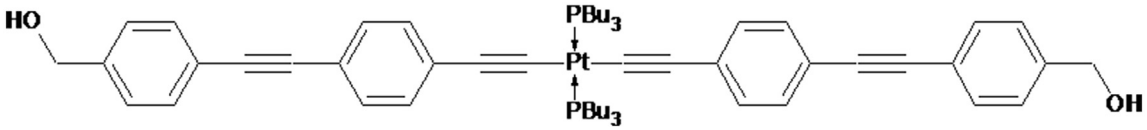

Fig. 1. Structure of PE2-CH_2OH.

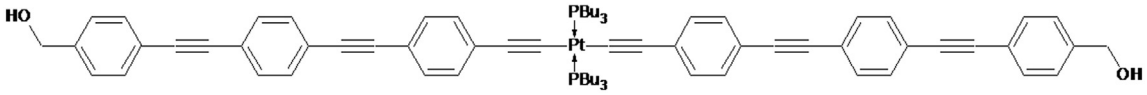

Fig. 2. Structure of PE3-CH_2OH.

of either spherical or bipyramidal AuNPs, the glasses showed enhanced NLA at 600 nm excitation wavelength, but no enhancement at 532 nm [5]. The enhanced NLA efficiency at 600 nm was explained by an increased two-photon absorption (2PA) due to field enhancement by the AuNPs [5]. The stronger 2PA caused the highly absorbing triplet state to not only increase its population, but also to be populated earlier during the 5 ns laser pulse [5].

An alternative platinum(II) acetylide, PE3-CH_2OH (Fig. 2), has shown stronger non-linear absorption than PE2-CH_2OH [1]. In both cases the $-CH_2OH$ functionalization is used to improve solubility of the chromophore during the sol-gel preparation process [1]. Both PE2 and PE3 in solutions have been characterized previously [4,13,14]. The excited state absorption (ESA) for both PE2 and PE3 in the 532–600 nm range is similar at about $2–5 \times 10^4\ M^{-1}\ cm^{-1}$ [14]. PE2 and PE3 in solution have triplet lifetimes around 42 and 86 μs respectively [14]. In MTEOS glasses the phosphorescence lifetimes of both PE2-CH_2OH and PE3-CH_2OH is in the order of microseconds [1]. In solution, PE3 has a stronger 2PA cross-section compared to PE2, 740 GM versus 290 GM [4,13]. The ISC time of PE2 is approximately 300 ps [4], while the ISC time for PE3 has been reported to be shorter at 19.5 ± 2 ps [13].

In this work, we systematically investigated PE3-CH_2OH co-doped with AuNPs of different shapes and concentrations. Both spheres and bipyramids were used since bipyramids are expected to produce large field intensities near their tips that could impose non-linear effects [15]. A range of different AuNP concentrations were tested, since the 2PA enhancement might be counteracted by linear absorption ahead of the focus in the glass [5]. The PE3-CH_2OH doped glasses were compared to the PE2-CH_2OH and/or AuNP doped glasses previously reported. Simulations based on a population model are used to explain and discuss the results.

2. Material and methods

Methyl triethoxysilane (MTEOS, 98%) and aminopropyltetraethoxysilane (APTES, 97%) were purchased from Gute Chemie, abcr GmbH. HCl (37%), triethylamine (97%), ethanol (99.8%), Tetrahydrofurane (THF, 99%), diethyl ether, citric acid (99%), cetyltrimethylammonium chloride (CTAC) 25% in water, 8-hydroxyquinoline (HQL, 99%), $NaBH_4$ (99.999%) and NaOH (98%) were purchased from Sigma-Aldrich and used as received. $HAuCl_4$, $3H_2O$ (99.9%), and silver nitrate (99.9%) were purchased from Alfa Aesar.

2.1. Synthesis of gold nanospheres

Spherical gold nanoparticles were synthesized using procedures reported earlier [12]. Seed mediated growth was used to obtain nanoparticles with low polydispersity. The gold seeds were synthesized by quickly adding 400 μL of freshly prepared mixtures of $NaBH_4$ 50 mM/NaOH 50 mM into a solution of 32 mL cetyltrimethylammonium chloride (CTAC 66 mM), 320 μL of $HAuCl_4$ (25 mM in water) and 296 μL of HNO_3 (0.25 M) under stirring. The solution was heated at 80 °C for 50 min. A growth solution containing 600 μL of CTAC and 200 μL of $HAuCl_4$ (25 mM) in 19.4 mL of Milli-Q purified water was prepared. This mixture was stirred for 15 min at 60 °C and 150 μL of 8-hydroxyquinoline (HQL 0.4 M in THF) was added. Finally, the spherical AuNPs were obtained by adding the appropriate amount of seeds to the growth solution. The final size of the AuNPs is directly related to the amount of seeds added in this step. For example, adding 120 μL of the seeds solution to the growth solution generates 45 nm AuNPs. A transmission electron microscopy (TEM) image of these spherical AuNPs is shown in Fig. 3.

2.2. Synthesis of gold bipyramids

Synthesis of bipyramid AuNPs using the seed mediated process has been reported previously [5,12,16–18].

2.2.1. Synthesis of the seeds

100 μL of NaBH4 solution (50 mM $NaBH_4$ and 50 mM NaOH) was added, under stirring at 20 °C, to the following mixture: 4 mL $HAuCl_4$ (0.5 mM), 4 mL CTAC (95 mM) and 72 μL HNO_3 (250 mM). Then, 16 μL of citric acid (1 M) was added to the mixture which was heated to 80–85 °C for 60 min in closed vials in a water bath.

2.2.2. Growth of gold bipyramids

The growth solution was composed of 40 μL of $HAuCl_4$ (25 mM/water) and 4 mL CTAB (47 mM/water). 18 μL of silver nitrate solution in water (10 mM) and 40 μL of 8-hydroxyquinoline in ethanol

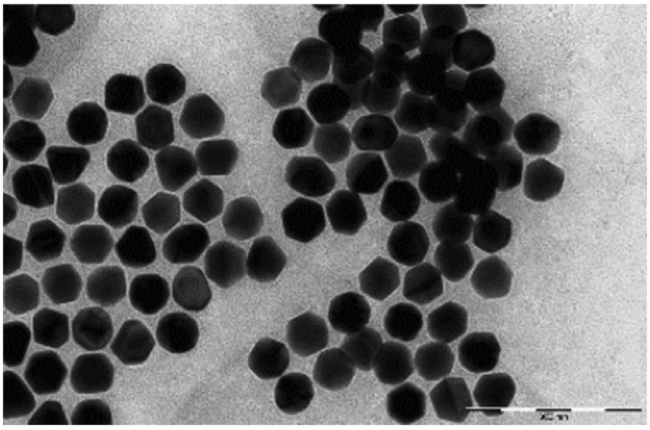

Fig. 3. TEM image of 45 nm diameter spherical AuNPs (Scale bar 200 nm).