



Enhanced two-photon absorption property of silver nanoparticle aggregates induced by a thioether derivative



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ABSTRACT

A novel thioether derivative with two-photon absorption activity, 4,4'-((4-(dimethylamino)phenyl)methylene)bis(sulfanediy) dianiline (abbreviated as **L**), was designed and synthesized, which was used to couple with Ag nanoparticles (Ag NPs, ~6 nm) to construct **L**-Ag hybrid particles with **L** uniformly dispersed on the surface of Ag NPs. The newly-formed hybrid particles self-assembled through **L**-**L** interactions between **L** molecules in one hybrid particle and adjacent particle to form Ag NPs aggregates (100 nm in diameter). By Raman and XPS analysis, the interfacial interaction 'hot spot' was determined, which was between thioether group and primary amino group of **L** molecule and Ag⁺ ion on the surface of pure Ag NPs. The interfacial interactions between the two components brought about changeable linear optical properties and enhanced nonlinear optical properties, two-photon absorption cross section and two-photon absorption coefficient included. Furthermore, the optical power limiting application of Ag NPs aggregates was also optimized by this means.

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1. Introduction

Over the past few decades, the development of materials with large two-photon absorption (TPA) cross-section (δ) has drawn great interest, because of a number of promising applications in photonics and optoelectronics including optical power limiting [1], frequency up-converted lasing [2], 3D optical data storage [3], fluorescence bio-imaging [4], 3D microfabrication [5], photodynamic therapy [6], and so on. With these considerable potential applications, a large number of materials with large δ value and good processibilities have been developed, such as inorganic fluorescent materials (semiconductors, metallic nanoclusters, rare earth luminescent materials), organic fluorochrome and organic-inorganic fluorescent hybrids. Among inorganic nanomaterials, the noble metal such as Au and Ag have become one of hot researches, due to their fascinating properties and applications in catalysis [7], electronics [8], photography [9], information storage [10], sensing [11], bio-imaging [12], and so on. It is known that noble metal nanomaterials with tiny size possess excellent optical properties, especially linear/nonlinear fluorescent emission for

metallic nanoclusters. However, these cluster particles in tiny scale cannot exist normally, which must be modified with protective agent. If the protective agent is an organic functional ligand, organic-inorganic hybrids with changeable or optimized character will be organized.

Organic-metal hybrids consisted of organic functional ligand and noble metal nanoparticles offer possibilities for enhancement of optical responses, such as metal-enhanced fluorescence (MEF), surface-enhanced Raman scattering (SERS) and/or enhanced two-photon excited fluorescence (TPEF) as mentioned above, partly due to the localized surface plasmon (LSP) of metal NPs and the enhanced electromagnetic field intensity localized at the interface [13–15]. Several groups have devoted to investigate the two-photon absorption properties of Ag NPs capped with different organic molecules. The enhancement of the two-photon absorption has been observed in a few of hybrids. Marder et al. reported thiol-bound supramolecular self-assembled on Ag core and the resulting aggregated nanoparticles had an effective increased δ to that of the individual chromophores [16]. Perry et al. reported the enhanced TPA properties of silver clusters coated with chromophoric polymer or thiol-bound chromophores through noncovalent and/or covalent bond at the interface [17]. In our previous work, we reported the enhancement of the second- and third-order nonlinear optical susceptibilities (TPA included) of Ag NPs modified with carbazolyl

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styryl terpyridine [18] and fluorophore-phenylamine [19] through weak interfacial interactions. However, to the best of our knowledge, thioether derivatives modified Ag NPs has scarcely been studied, not to say the TPA character of them. According to hard and soft acid-base principle, Ag^+ ions on the surface of Ag NPs tend to act with S atom of thioether derivatives, which will benefit for construction of thioether derivative-Ag nano hybrids. The interactions between Ag^+ ions and S atom at the interface will change the electron distribution of both Ag^+ ion and the organic ligand, to some extent, which are expected to bring about changeable, even enhanced optical properties.

Considering all the above aspects, a novel thioether derivative 4,4'-((4 (dimethylamino)phenyl)methylene)bis (sulfanediyl) dianiline (**L**) was synthesized, which was designed as a surface modification agent and optical properties regulator. Based on the energy level matching effect, Ag NPs at a mean diameter of about 6 nm was used to couple with **L** and construct **L**-Ag hybrid particle with Ag NPs as the core and **L** molecules as the shell. Furthermore, self-assembled of the hybrid particles into 100 nm Ag NPs aggregates occurred due to the interactions between **L** molecules in one **L**-Ag hybrid particle and adjacent particle. The coupling effect between the two components and the corresponding self-assembly process not only had a profound impact on the adjustment of the changed morphology and the single photon optical properties, but also resulted in the enhancement of two-photon absorption properties, including TPA cross section (δ) and TPA coefficient (β). The increased TPA character was successfully used in optical power limiting application.

2. Experimental

2.1. Synthesis of **L**

The synthetic route of **L** was listed as Scheme 1. For preparing **L**, 4-(dimethylamino)benzaldehyde (1.0 g, 6.7 mmol) was dissolved in 50 mL of ethanol and 4-aminobenzenethiol (1.98 g, 15.8 mmol) was added into it. Then 8 drops of acetic acid were added as catalyzer. Afterward, the mixture was refluxed for 12 h. After the reaction, yellow solids were precipitated and then the mixture was cooled down to room temperature. Finally, the as-obtained precipitate were washed with excess ethanol for three times and dried in vacuum oven to get the target compound **L** [20,21]. Yield: 85%. FT-IR (KBr, cm^{-1}): 3369, 3383, 3069, 2934, 1640, 1600, 1500, 1346, 1084, 820, 697. ^1H NMR (DMSO- d_6 , 400 MHz): δ (ppm): 7.07 (d, 2H, $J = 8.3$ Hz); 6.96 (d, 4H, $J = 8.0$ Hz); 6.57 (d, 2H, $J = 8.4$ Hz); 6.43 (d, 4H, $J = 8.0$ Hz); 5.254 (m, 4H); 5.090 (s, 1H); 2.86 (m, 6H). ^{13}C NMR (DMSO- d_6 , 100 MHz): δ (ppm): 149.57, 148.99, 135.15, 128.49, 127.44, 118.24, 113.97, 111.59, 62.16, 39.53. HR-MS (ESI $^+$, 4.5 KV, 200 °C) $m/z = 380.1243$ [M-H] $^+$, calcd for $[\text{C}_{21}\text{H}_{23}\text{N}_3\text{S}_2]^+ = 381.13$ [M] $^+$.

2.2. Preparation of **L** nanostructures

L nanostructures were prepared through recrystallization method [22]. In this experiment, 200 μL (1.0×10^{-3} mol L^{-1}) of **L** ethanol solution was injected into 2 mL pure deionized water under

stirring. Then, the mixed solution was stirred about 10 min and stayed still for 12 h at room temperature.

2.3. Preparation of Ag NPs aggregates

Pure Ag NPs with the size being ~ 6 nm were prepared referenced the reported literature [23]. For preparing Ag NPs aggregates, 1 mL of pure Ag NPs in cyclohexane (0.346 mg/mL) solution was mixed with 3 mL of **L**-ethanol solution (with different concentrations) at room temperature (the mass ratio of **L** to Ag was changed from 3:1 to 9:1). Then, the mixture was exposed to a mild shaking at 800 rpm for 5 min, 45 min, 1 h, 2 h, 4 h, respectively and Ag NPs aggregates were obtained after washed with excess ethanol and dried in vacuum oven. Then, the as-obtained Ag NPs aggregates were dispersed in 2 mL ethanol for further detection and optical measurements.

2.4. TD-DFT calculation

Molecular orbital calculations of time-dependent density functional theory (TD-DFT) at the B3LYP/6-31 g level basis set (Gaussian 03) [24] were performed to study the electronic structures of **L** molecule and the corresponding energy level matching between **L** and Ag components.

3. Results and discussion

3.1. The morphology of the materials

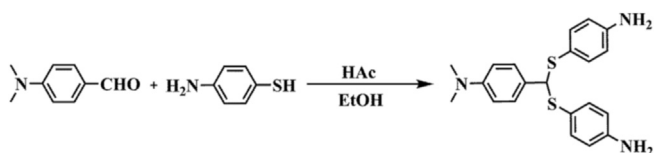
3.1.1. The morphology of free **L** and pure Ag NPs

Free **L** nanostructures were simply prepared from **L**-EtOH solution through re-crystallization method without addition of surfactant, template or catalyst [25]. The SEM image of **L** nanostructures was shown in Fig. 1a. The results indicated that the shape of **L** was multiple ball together and the size of which was about 200–400 nm. The morphology of pure Ag NPs was shown in Fig. 1b and c. The as-prepared pure Ag NPs were highly mono-dispersed spherical shape with the mean size being about 6 nm. The HRTEM image (Fig. 1c) revealed the structural information of the initial Ag NPs and the lattice fringes with distance of 2.28 Å corresponded to the {111} planes of face-centered cubic (FCC) Ag NPs [26]. DLS analysis showed the particle size ranged from 4.6 nm to 7.8 nm with the average value being approximately 6 nm (Fig. 1d), agreed well with that of TEM analysis.

3.1.2. The morphology of Ag NPs aggregates

The ratio of **L** to Ag showed a significant influence on the morphology of Ag NPs aggregates. When the ratio was 3:1, Ag NPs appeared the signs of aggregation comparing to pure Ag NPs (Fig. 2a). As shown in Fig. 2b, when the ratio of **L** to Ag was 6:1, more Ag NPs arranged together. Some aggregated particles with regular morphology appeared with some dispersed Ag NPs dissociated outside of the aggregates. The average diameter of the aggregated particles was 60–70 nm. When we prepared Ag NPs aggregates according to the mass ratio of **L** to Ag being 9:1, Ag NPs were aggregated well. The aggregated Ag NPs had regular spherical morphology with clear boundary to each other, the average diameter of which was about 100 nm (Fig. 2c and e).

The phenomenon observed above revealed that the state of aggregation for Ag NPs was tremendous affected by the existence of **L**. In detail, when **L** was added to the mixed solution, Ag^+ on the surface of Ag NPs may act with primary amine and/or thioether group of **L** through N and/or S atom. Thus, **L** molecules were adhered to the surface of the Ag NPs to form **L**-Ag hybrid particle with Ag NP as the core and **L** as the shell. Then, the weak



Scheme 1. The synthetic route of **L**.

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