

Nonlinear Optical Properties of Gold Nanoparticles/Polymer Hybrid Materials

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ABSTRACT

It is well known that the properties of nanostructured materials are not only dependent on the size and the function of the individual nanoparticles itself, but also the interparticle distances and interactions. Recently our group reported a solid phase exchange reaction to synthesize gold nanoparticles with a single carboxyl functional group on the surface. Using these monofunctional gold nanoparticles, we synthesized a nanoparticle-polymer hybrid material with a necklace structure using a single step chemical reaction. The optical limiting performance of the gold nanoparticles-polymer hybrid was then investigated using a 4.1 ns laser at 532 nm. The hybrid materials exhibited enhanced optical limiting properties compared to individual monofunctional gold nanoparticles due to the dipole-dipole interparticles interactions. It was also found that the triplet excited state absorption was the main contribution to the optical limiting properties of the nanoparticles/polymer hybrid materials.

Keywords: nonlinear optical optics, gold nanoparticles, polylysine, hybrid, necklace structure

1 INTRODUCTION

Organization of gold nanoparticle building blocks into well-defined arrays provides a means to impart the desirable properties for nanodevices fabrication.¹ Current research rests heavily on self- and templated-assembling approaches towards the fabrication of well-ordered nanostructured materials.² Although tremendous progress has been achieved in this field, there still remains significant limitation of self-assembled nanomaterials. For example self-assembled nanomaterials are often not sufficiently stable because the weak noncovalent interactions can be disrupted by dissolution, pH change, or heating. To address this challenge, our group recently developed a novel solid phase place exchange reaction to synthesize gold nanoparticles with a single functional group on the surface.^{3,4} Using these molecular nanobuilding blocks, we synthesized sophisticated nanoparticles/polymer hybrid materials by chemical reactions of nanoparticles with polymer templates. The nonlinear optical properties of such hybrid materials were investigated.

2 EXPERIMENTAL

2.1 Materials

All solvents and organic chemicals were purchased from Aldrich (Milwaukee, WI) or VWR (West Chester, PA), except the following items: gold salt HAuCl₄ · H₂O was purchased from Strem Chemicals (Newburyport, MA). Sephadex gel LH-20 used in gel permeation chromatography (GPC) was purchased from Sigma with a separation limit of 7000 Dalton molecular weight.

2.2 Instrumentation

TEM images were obtained from a FEI Technai F30. The electronic absorption spectra were measured using an Agilent 8453 UV-Vis spectrophotometer. The transient difference absorption was investigated using an Edinburgh LP920 laser flash photolysis spectrometer. The optical limiting measurements were carried using 4.1 ns laser pulses at 532 nm. A Q-switched Quantel Brilliant Nd: YAG laser was used as the light source. The repetition rate of the laser was set to 10 Hz.

2.3 Synthesis of Monofunctional Gold Nanoparticles/Polylysine Hybrid

Monofunctional gold nanoparticles were prepared according to the reported procedure.⁵ Polylysine (0.5 mg/mL, 100 µL in methanol, MW: 93,800) solution was mixed with monofunctional gold nanoparticles (1.0 mg/mL, 400 µL in dichloromethane/methanol, 1/1) solution, followed by the addition of diisopropylcarbodiimide (DIPCDI) (40 µL). The reaction mixture was shaken at room temperature for 2 hours. The precipitates and the solution were separated by centrifugation. The precipitates were washed with methanol for several times to remove unreacted polylysine.

3 RESULTS AND DISSCUSSION

Recently we proposed an alternative approach for assembling the nanobuilding blocks together with precisely

well-controlled structures using covalent bonding chemistry. A solid phase synthesis technique was used to prepare monofunctional gold nanoparticles.^{3,4} With a single functional group attached on the surface, such nanoparticles building blocks may be treated as “molecules” and used to react with polymer scaffolds to form extended nanostructure through simple chemical reactions.

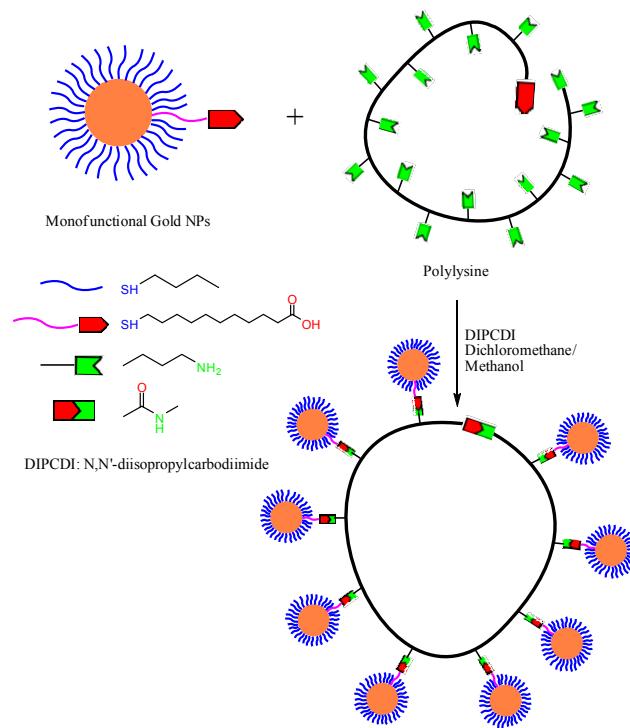


Figure 1: schematic illustration of a“nanonecklace” assemblies of monofunctional gold nanoparticles/polylysine hybrid materials.

To demonstrate the potential of this strategy, we used single carboxyl functionalized 2 nm gold nanoparticles to react with polylysine in the presence of an amide coupling agent (DIPCDI) (Figure 1). Polylysine is a linear polypeptide with amino groups on the side chain. The single carboxyl functionalized gold nanoparticles were reacted with polylysine to form amide bonds between the side amino groups and nanoparticles. During the reaction, it was also observed that an intramolecular cyclization reaction occurred between the carboxyl acid end group and one of the amine groups extending from polylysine chain, which resulted in the formation of a “nanonecklace” structure (Figure 2). UV-Vis absorption spectra of “nanonecklace” nanoparticles/polylysine hybrid materials showed a clear red shift of the surface plasmon resonance band in comparison with the isolated monofunctional gold nanoparticles (Figure 3). In a control experiment, we used a Boc-protected ethylenediamine molecule to block the carboxyl end group of the polylysine. The blocked polylysine was then coupled with single carboxylic functionalized gold nanoparticles. TEM analysis of this

coupled product did not show any evidence of nanonecklace structure, but instead, some linear chain aggregates of nanoparticles were found.

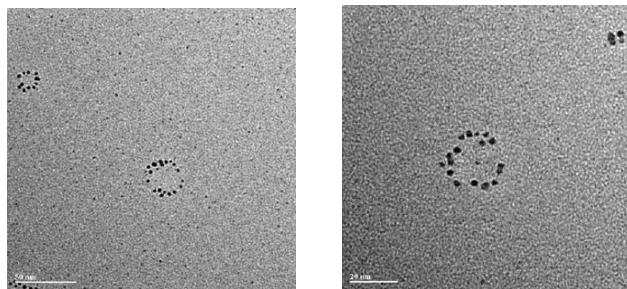


Figure 2: TEM images of nanonecklace-like gold nanoparticles/polylysine hybrid materials.

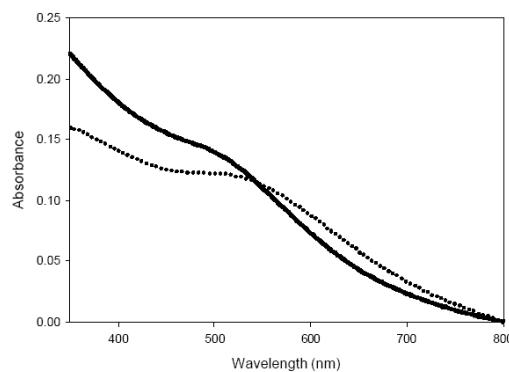


Figure 3: UV-vis absorption spectra of nanonecklace-like gold nanoparticles/polylysine hybrid materials in 1:1 CH₂Cl₂: CH₃OH with 1% trifluoroacetic acid (solid line: monofunctional gold nanoparticles, dotted line: gold nanoparticles/polylysine hybrid materials). (Reprinted with permission from ref 5 Copyright 2005 American Chemical Society.)

Gold nanoparticles have been known for their optical limiting properties when they are assembled into aggregates due to the surface plasmon coupling interaction between the adjacent nanoparticles. We investigated the nonlinear optical properties of gold nanoparticle-polylysine hybrid material using an Nd: YAG laser (4.1 ns pulse at 532 nm) as irradiation source. From the nonlinear transmission measurement in Figure 4, it is observed clearly that the hybrid material shows a significantly increased optical limiting in comparison with the individual free nanoparticles. The transmission of hybrid material drops from 70% to 25%, when the incident fluence is up to 1.7 J/cm². However the transmission of individual nanoparticles decreased only to 50% with an incident fluence of 1.7 J/cm². Because the pure polylysine backbone has no absorption at 532 nm, therefore the optical limiting enhancement behavior of hybrid material could be ascribed to the surface plasmon intercoupling between neighboring nanoparticles.

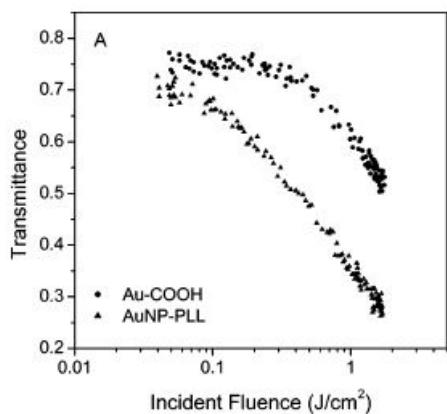


Figure 4: Optical limiting curves of nanonecklace-like gold nanoparticles/polylysine hybrid in 1:1 CH₂Cl₂: CH₃OH with 1% trifluoroacetic acid. (Reprinted with permission from ref 6. Copyright 2005 American Chemical Society.)

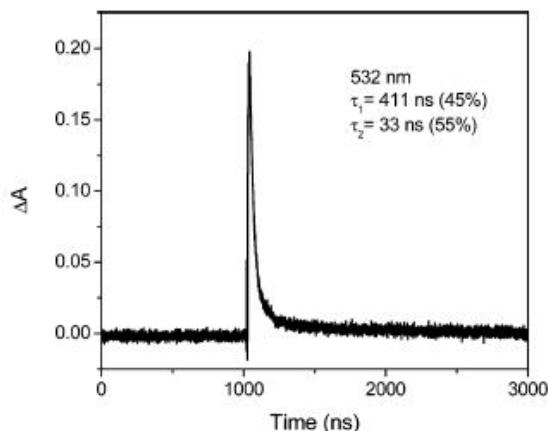


Figure 5: Transient absorption decay profile of nanonecklace-like gold nanoparticles-polylysine hybrid in 1:1 CH₂Cl₂: CH₃OH with 1% trifluoroacetic acid. (Reprinted with permission from ref 6. Copyright 2005 American Chemical Society.)

Further investigation in the transient absorption spectroscopy (Figure 5) shows a positive peak due to the increasing of the excited-state absorption coefficient at 532 nm in comparison with that of the ground-state absorption. This result suggests that the optical limiting enhancement of hybrid material is a result of reverse saturable absorption (RSA). Free-carrier absorption (FCA) may also be contributed to the optical limiting enhancement when the free electron on the surface of gold nanoparticles was excited. It is observed in Figure 5 that the transient absorption of hybrid material contains a faster component of 33 ns and a slower process of 411 ns, which are long enough for RSA and FCA process to occur. Therefore it is reasonable to believe that reverse saturable absorption and free-carrier absorption could be the main reason for the optical limiting enhancement of hybrid material.

4 CONCLUSIONS

In summary, a gold nanoparticle/polylysine hybrid material was synthesized by covalent attachment of single carboxylic group functionalized gold nanoparticles to a polylysine backbone, followed by ring closure of the polylysine chain in the presence of an amide coupling agent, (DIPCDI). The enhanced optical limiting properties of the gold nanoparticles/polylysine hybrid material are attributed to the electromagnetic interactions between the neighboring nanoparticles. Reverse saturable absorption and/or free carrier absorption are the main contributor(s) to the optical limiting enhancement behavior of hybrid material.

5 ACKNOWLEDGMENT

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