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Morphology dependent two photon absorption in plasmonic structures and plasmonic–organic hybrids

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ABSTRACT

Two photon absorption coefficients of two distinct plasmonic structures, namely, gold nanoflowers (GNF) and gold nanopebbles (GNP) have been investigated and compared with conventional gold nanospheres (GNS). All three different nanoshapes were synthesized by changing the reaction solvent under the same experimental procedure. Further, hybrids of these plasmonic structures were prepared with an organic dye Eosin yellow (EY), to investigate the morphology effect of plasmonic structures on plasmonic–organic hybrids in terms of their linear extinction spectra and two photon absorption coefficients. The NLO investigations were conducted using 20 ps laser pulses of wavelength 532 nm as an excitation source in single beam Z-scan setup. UV/visible spectroscopy was employed for monitoring plasmon resonances and changes in linear extinction spectra. The experimental outcomes revealed two photon absorption coefficients of EY increased 120%, 32% and 39%, while 69%, 60% and 53% enhancement in the peaks of linear extinction maxima of EY has been observed, when hybridized with GNF, GNS and GNP, respectively. This boost in the optical coefficients may be attributed to dimerization of EY molecules on the surface of nanoparticles. Keeping the toxicity of EY in view, we propose that the two photon absorption coefficients of this dye and control thereof, by the addition of plasmonic structures would be helpful not only in understanding the interactions between plasmons and fluorophore, but also pave an efficient way, to reduce the operative concentration of this hazardous dye in a wide range of applications and thereby, mitigating the environmental degradation caused by its highly concentrated effluents.

1. Introduction

The distinctive ability of plasmonic structures to concentrate and manipulate photonic signals in deep sub-wavelength domain provide novel, efficient pathways to generate, guide, modulate and detect light [1–7]. Due to collective oscillations exhibited by the conducting electrons of metallic nanoparticles, their local fields can be greatly enhanced at the localized surface plasmon (LSP) resonance [3]. Hence, plasmonic structures offer a versatile platform where LSPs can be tuned over a broad range of wavelengths by controlling their shape, size and material properties. The linear optical properties of nanoparticles are currently being exploited for a variety of applications including molecular sensing [8,9], tagging [10,11], focusing of light [12,13], as well as sub-wavelength photonics [14,15]. Unlike linear behavior, an understanding of the nonlinear optical (NLO) properties of metallic nanostructures is still in its infancy, with no general conclusion on the relationship between them. When exposed to high-intensity illumination, metallic nanoparticles unveil a wide range of NLO responses, which include photo thermal reshaping [16,17], second harmonic generation [18–20] and third order optical nonlinearities [21–25]. The nonlinear absorption and nonlinear refractive index are very important parameters in designing photonic devices. The single beam Z-scan method with the advantage of separating the contributions of refractive and absorptive nonlinearities in the samples which was originally proposed by Sheik-Bahae et al. in 1989 [26] has become a standard tool for the measurement of these nonlinear coefficients due to its high sensitivity and its ability to immediately indicate the sign and type of nonlinearity. Since then, this technique has been extensively used in contemporary photonic technologies [7,22,24–26]. Conventionally optical nonlinearities are inherently weak, as they directed by photon–photon interactions inside the materials. They super-linearly rely on the electromagnetic field and can be enhanced in material environments which provide mechanisms for field strengthening [20,27–29]. Thereby, interactions between localized plasmons and organic molecules have gained interest as they form the basis for developing and realizing a wide range of technological applications such as surface enhanced Raman spectroscopy [8,30], plasmon-enhanced fluorescence [31], amplification of nonlinear optical signals

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[32], nanoscale lasers [33], plasmon-assisted photolithography [34,35], plasmon-enhanced solar light harvesting [36,37] and ultra-sensitive chemical and biological sensors [38,39].

Eosin yellow (EY), 2-(2,4,5,6-Tetrabromo-6-oxido-3-oxido-3H xanthenes-9-yl) is a fluorescent organic dye, conventionally used in the fields of dyeing, printing, leather and fluorescent pigment etc. Eventually, this dye has been identified hazardous and toxic in nature [40–42] as the high concentration of dye effluents results in the formation of toxic wastewaters with low light transparency and high inorganic carbon content. Moreover, the molecules of EY are highly stable to light and heat exposure, due to which chemical or physical methods are unable to biodegrade the dye completely [43]. Despite its toxic response, optical properties of EY are widely studied and utilized for several applications. Its tendency to bind with basic proteins, in vivo and thus, providing different colors to the stained cells or to tissues finds application in multidimensional non-linear laser imaging of cell carcinomas [44] and multi-contrast microscopy of histological sections and hematology [44,45]. Huge π conjugated structure allowing low energy π-π* transitions i.e. in the visible part of the spectrum, makes it an effective photo-catalyst [46,47]. Owing to its fluorescent properties, EY is used in the fabrication of holographic optical elements [48]. The literature supports that Eosin is one of the potential candidate (as a dye) in molecular-based photovoltaic devices with higher overall energy conversion efficiency [49,50]. The third order nonlinear optical switching study of EY using nanosecond pulses and self diffraction of eosin doped thin films have also been reported [51,52]. While, many promising applications of the dye-nanoparticle hybrid have been exploited, a detailed understanding of interparticle interactions and two photon absorption coefficients, especially in cases involving dye mediated assemblies are rarely reported.

This paper presents two photon absorption and refractive index coefficients, of the two distinct plasmonic structures, namely, gold nanoflowers (GNF) and gold nanopebbles (GNP) along with their comparison with the conventional gold nanospheres (GNS). In order to better understand the morphology effect of plasmonic structures on the two photon absorption coefficients of nanohybrid structures, we experimentally evaluated the nonlinear absorbance and nonlinear refractive index coefficients of three different gold nanoshapes, a commercially important dye (EY), and their hybrids i.e. EY-GNF, EY-GNP and EY-GNS using picosecond laser pulses of wavelength 532 nm as an excitation source in the standard single beam Z-scan setup.

2. Experimental section

2.1. Chemicals and reagents

Hydrogen tetrachloroaurate(III) hydrate ($HAuCl_4{\cdot}3H_2O$), Triethanolamine (TEA) [$(HOC_2H_4)_3N$] [$C_6H_{15}NO_3$] and ethylene glycol (EG) [$C_2H_6O_2$] were procured from Sigma Aldrich chemicals, USA. Additionally, EY (Mol. Wt.–691.86) was purchased from Qualigens fine chemicals division, Thermo Scientific Pvt. Ltd., India. Other analytical grade chemicals and reagents used in the experiments were utilized as received without any further purification. Deionized water obtained through Milli Pore (Scholar-UV Nex UP 1000) water purification system was used for the preparation of aqueous stock solutions and their dilutions.

2.2. Preparation of gold nanostructures and EY-gold nanostructures

Gold colloids were synthesized using Jiang et al. method with some modifications [53]. All three different nanoshapes were synthesized, by changing the reaction solvent under the same experimental procedure. 200 µl of aqueous $HAuCl_4$ (1 wt%) solution was added to 20 ml of pure EG in a 60 °C water bath. Then 400 µl of freshly prepared TEA solution with concentration 2.5 M was added in four steps with mild stirring and the reaction was allowed to run for 60 min. To gain the effect on the final size and morphology of gold nanostructures, other solvents such as pure water and a mixture of EG and water [1:1 (v/v)] were separately examined. Further the gold nanoparticles prepared using three different reaction solvents namely EG, pure water and a mixture of ethylene glycol and water (1:1 (v/v)) were centrifuged and washed three times at 12,000 rpm for 20 min and redispersed in deionized water for further analysis.

For the preparation of EY-gold hybrids, 5.78 mM EY stock solution was prepared by dissolving 2 mg of dye into 500 µl of ethanol. Then, hybrids were prepared by addition of different concentration of colloidal gold nanostructures to EY solution. The assembly was allowed to stand overnight before further investigations were conducted.

2.3. Instrumentation

2.3.1. X-ray diffraction

X-ray powder diffraction (XRD) analysis of the prepared gold colloids was done using Bruker D8 Advance Diffractometer, equipped with a monochromatic high-intensity Cu-Kα X-rays of wavelength (λ) 1.5432 Å. Data were taken over the (10–80°) range with a step size of 0.02°.

2.3.2. High resolution-transmission electron microscopy (HR-TEM)

TEM micrographs were obtained using a FEI-Tecnai G^2 F30-STWIN instrument, using 300 kV electron acceleration voltage with field emission electron source. Samples for TEM analysis were prepared by drop wise addition of the gold colloidal solution on carbon-coated Cu-TEM grids (ultra-thin carbon film supported by a 3 mm copper grid). The film on the grid was allowed to stand for some time in order to facilitate the liquid evaporation. After drying, the specimen was transferred in the microscope column for imaging at different magnification and electron patterns were recorded.

2.3.3. UV/visible spectroscopy

Extinction spectra of gold colloids were obtained employing Perkin Elmer Lambda-35 spectrophotometer. The UV/visible spectrophotometer was calibrated using Normal Transmittance–Didymium Oxide filter (WC-DD-02c) traceable to the National Institute of Standards and Technology (NIST), USA, with a precision management of less than ± 0.2 nm wavelength shift and ± 0.5 A absorbance variation. For spectral acquisitions of the sample, a quartz cell having a path length of 1 cm was used in a scan range of 200–700 nm. Eosin solution of constant concentration (25 µM) was used, where different gold nanoparticles-EY ratios (v/v) 1:1, 1:2, 1:4, 1:8 and 1:10 were prepared with gold nanoshapes for UV/visible spectroscopic studies.

2.3.4. Closed and open aperture Z-scan

The nonlinear optical properties of the gold nanostructures and their hybrids were investigated using the standard Z-scan technique. The experimental setup comprised of a mode locked Nd:YAG laser with a frequency doubled at 532 nm, characterized by a pulse duration of 20 ps with a repetition rate of 1 kHz and pulse energy 0.34 mJ. The measured beam waist (ω_0) of the light source was 16 ± 1 µm. The polarized Gaussian laser beam was focused using 200 mm focal length lens into the sample which was placed in 1 mm path length quartz cuvette. At each position, the sample experiences a different light intensity. The light intensities transmitted across the samples were measured as a function of the sample position in the Z-direction with respect to the focal plane, through a 0.5 mm aperture (closed aperture) and without aperture (open aperture). On-axis transmitted beam energy, the reference beam energy as well as their ratios were measured using silicon photo diodes and collected using a calibrated digital multimeter. The sample movement was performed on a translation stage. The setup was optimized using the standard CS_2 solution. Eosin solution of constant concentration (100 µM) was optimized. Three different molar ratios (r) 1:1, 1:2 and 1:4 of EY were prepared with