Optical Materials 73 (2017) 83–88

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Size and structure dependent ultrafast dynamics of plasmonic gold nanosphere heterostructures on poly (ethylene glycol) brushes

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ARTICLE INFO

Article history:
Received 5 November 2016
Received in revised form
5 August 2017
Accepted 7 August 2017

Keywords:
Ultrafast dynamics
Gold nanospheres
Heterostructures
Plasmonics
Polymer brushes
Ultrafast pump-probe spectroscopy

ABSTRACT

We have investigated the plasmonic properties of heterostructures that consist of gold nanosphere (NSs) with average diameters of 60 nm, 40 nm and 20 nm on poly (ethylene glycol) (PEG) brushes by using ultrafast pump-probe spectroscopy experiments. Gold NSs start to behave like gold nanorods with increasing number of immobilization cycles due to the close proximity. Gold NSs immobilized by 3 and 5 deposition cycles show longitudinal modes of plasmon bands at long wavelengths which are characteristic behaviors for gold nanorods. Increasing the number of immobilization cycle also increase relaxation times of samples due to the close proximity. Linear absorption spectra and scanning electron microscopy images show that there are close packing assemblies for heterostructures containing 20 nm gold NSs as the small particle. Ultrafast electron transfer (<100 fs) occurs between transverse and longitudinal modes by exciting the samples at both 520 nm and 650 nm. Further, experimental results indicate that, heterostructures with the small particles have faster relaxation times than other heterostructures due to closed packing of 20 nm gold NSs.

Plasmonic metallic nanosphere (NSs) can be used in nanophotonic applications due to their high tunability of both linear and nonlinear optical properties by changing the size and structure of the particles [1–5]. Therefore, there is great interest in metallic NSs owing to excitation of the collective oscillation of conduction electrons which is termed as surface plasmon resonance (SPR) [6]. SPR leads to large local field confinement and enhancement. Especially, Au NSs and nanorods show an intense absorption band originating from the coherent oscillation of the nearly free conduction electrons induced by an interacting electromagnetic field [7]. Recently, Au nanorods have been prepared by electrochemical method [8] and electrodeposition of gold into porous alumina template [9–11]. The plasmon resonance split into two modes (i.e. transverse and longitudinal modes) and the wavelength of longitudinal modes can be tuned by changing the aspect ratio (length divided by the width) of nanorods. Therefore; changing the aspect ratio is an easy way to modify surface plasmon properties of nanorods. It was also reported that the characteristic time of Au nanorods to melt into nanodots by monitoring the disappearance of the characteristic longitudinal surface plasmon absorption. Very recently, it was observed that anomalously strong changes to the ultrafast temporal and spectral responses of the hot plasmonic electrons in hybrid metal/oxide nanostructure as a result of varying the geometry and composition of the nanostructure and the excitation wavelength [12].

For nanophotonic applications it is crucial to control the decay dynamics of hot electrons generated by the light excitation of metallic nanostructures. Nanostructures based on these effects are limited due to inadequate nanomanufacturing concepts. Varying size or spatial arrangement of NSs is common route in order to manipulate the plasmon resonance and collective optical properties of NSs. Enhancement of electromagnetic fields at subwavelength dimensions and localized SPR depend on the size, shape, material composition and structure of individual particles [1,2,13–18]. On the other hand, it is well known that symmetry-broken heterostructures attract attention due to their rich plasmonic properties such as asymmetric Fano resonances, nonlinear

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http://dx.doi.org/10.1016/j.optmat.2017.08.008
0925-3467/

optical properties and enhancement of electromagnetic fields [6,19,20]. Heterostructures present a highly suitable platform for nanophotonic applications, since the size, composition, structure and organization of the particles can be varied to generate nanostructures exhibiting a broad range of optical properties. It is extremely important to understand the decay dynamics of hot electrons in heterostructures to design nanostructures with suitable properties for different applications.

In the present work, we have studied optical properties, ultrafast dynamics and plasmon resonance of Au NSs assembled on poly(-ethylene glycol) (PEG) brushes by ultrafast pump-probe spectroscopy technique. PEG brushes allow for uniform and robust immobilization of colloidal Au NSs on substrates. A particular capacity of end-grafted PEG chains is assembly of NSs with different sizes into close-proximity configurations which we refer as heterostructures. This capability stems from the fact that citrate-stabilized Au NSs interact with PEG chains as a function of the size of the particle and the molecular weight of the polymer [20–22]. In this manner, one can focus on two important features of Au NSs. The first is the size and number of immobilization cycles of Au NSs and the second is heterostructures of Au NSs. The plasmon absorption is a sensitive tool to study the electron dynamics in Au NSs after excitation with femtosecond laser pulses. The interaction of light with Au NSs gives rise to inter- and intraband transitions of the metal electrons leading to a highly non-thermal distribution of electrons [23–25]. The selective excitation of the electron gas results in the broadening of the plasmon absorption band and transient bleach in the femtosecond pump-probe spectrum is observed [26–29]. The electron population then decays through electron-electron interactions (few hundred femtoseconds) and a further electron-phonon scattering (a few picoseconds). In such a study, it is possible to gain information changes of the ultrafast temporal and spectral responses of the excited electrons in Au NSs. Further, to the best of our knowledge, there is no work on explanation of ultrafast dynamics of heterostructure Au NSs by using ultrafast pump-probe spectroscopy technique in the literature. Therefore, we report here on the femtosecond electron dynamics of both Au NSs and heterostructure Au NSs on PEG with average diameters of 60 nm, 40 nm and 20 nm on PEG brushes.

1. Experimental methods

1.1. Sample preparation

Silicon wafers <100> were purchased from Wafer World Inc. Glass slides were purchased from Isolab Inc. PEG (35.0 kg/mol, Bio-Ultra) was purchased from Sigma-Aldrich. Chlorobenzene, chloroform and ethanol were purchased from Merck. Au NSs (20 nm, 40 nm and 60 nm in diameter) were purchased form Ted Pella Inc. Water was purified with a purification system.

We cleaned all substrates (silicon wafers and glass slides) in UV-ozone chamber (Bioforce, procleaner) for 20 min. We prepared two types of substrates: Si substrate (for thickness measurement) and Glass slide (for optical characterization). We deposited a film of PEG on the freshly cleaned substrate by spin-coating (Laurell) from a solution (2%) in chlorobenzene at 3000 rpm for 30 s. After then we annealed the PEG films at 180 °C on a hot-plate in a glove box filled with argon, at an oxygen and moisture level lower than 0.1 ppm and 0.5 ppm, respectively. Subsequent to the annealing, we washed the substrate with sonication in chloroform 3 times for 3 min per cycle and then dried by blowing nitrogen. The thickness of the PEG brushes was measured by using a Gaertner LSE Stokes Ellipsometer. Au NSs were immobilized by spotting a solution of the particles on the PEG grafted substrate in a humidified environment followed by washing for 2 min in water under sonication and drying with nitrogen. The surface morphology of the NSs nanostructures was imaged with a SEM (Zeiss EVO LS10) at 20 kV.

1.2. Optical measurements

The absorption spectra of the investigated crystals were taken by using a UV–Vis absorption spectrophotometer (Shimadzu UV-1800). Transmission pump-probe spectroscopy technique is used to understand ultrafast dynamics of Au NSs on the PEG brushes with the help of Ti:sapphire laser amplifier optical parametric amplifier system (Spectra Physics, Spitfire Pro XP, TOPAS) with 100 fs pulse duration. The excitation wavelength was chosen as 520 nm and 650 nm for the pump-probe experimental setup with white light continuum as a probe beam (Spectra Physics, Helios).

2. Results and discussion

Heterostructures that consist of Au NSs of different sizes are fabricated by immobilization of pre-synthesized colloidal particles on substrates functionalized PEG brushes (Fig. 1). SiOx terminated silicon and glass substrates are functionalized by grafting of PEG molecules through the condensation reaction between the hydroxyl functionality of the polymer and silanol groups of the substrates.

The citrate-stabilized Au NSs of different sizes (60 nm, 40 nm, 20 nm) were then immobilized on the PEG brush grafted substrates. To generate heterostructures of Au NSs, particles of different sizes were sequentially deposited on PEG brushes. The deposition started with the larger particle followed by the small particle. Each deposition step involved spotting the solution of citrate-stabilized Au NSs followed by washing in water and drying. The number of deposition steps for each particle varied as 1, 3 and 5.

The linear absorption spectra of both Au NSs and heterostructures of Au NSs on PEG brushes are given in Fig. 2. As seen from Fig. 2, two plasmon absorption bands have peaks around 520 nm and above 600 nm. The plasmon band which is placed around 520 nm corresponds to transverse surface plasmon resonances and also the plasmon resonances of spherical Au NSs absorb around 520 nm in an aqueous solution [26,30,31]. There is also another plasmon band around 680 nm for 20 nm and 60 nm Au NSs after 3 h immobilization process while the second plasmonic band of 40 nm Au NSs placed around 620 nm. In the literature, similar resonances bands were also observed for Au nanorods and attributed to

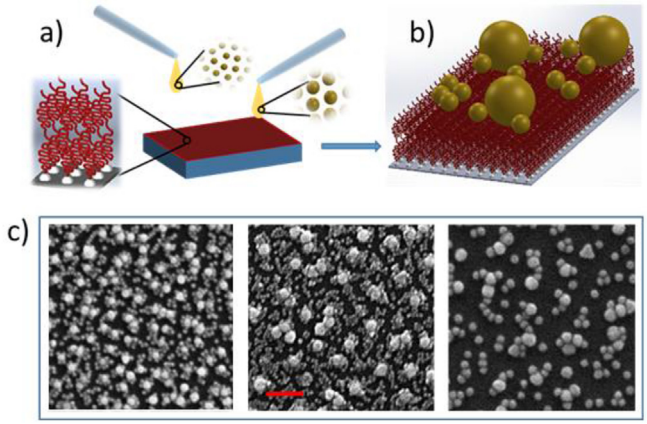

Fig. 1. Assembly of heterostructures on PEG brushes. a–b) Schematic description of the process. a) PEG brush grafted glass slides and silicon wafers serve as the substrate. b) Heterostructures are fabricated by sequential immobilization of the large and small Au NSs. c) A representative SEM images of the heterostructures that consist of Au NSs with diameters of 40 + 20 nm, 60 + 20 nm and 60 + 40 nm, respectively.