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Article

Studies of Ultrafast Transient Absorption Spectroscopy of Gold Nanorods in an Aqueous Solution

Garima Kedawat,^{*,†} Indu Sharma,[†] Kanika Nagpal,[†] Mahesh Kumar,[†] Govind Gupta,[‡]

[†]Photonic Materials Metrology Sub Division, Advanced Materials and Device Metrology Division and [‡]Sensor Device Sub Division, Environmental Science & Biomedical Metrology Division, CSIR–National Physical Laboratory, New Delhi 110012, India

S Supporting Information

ABSTRACT: Herein, ultrafast transient absorption spectroscopy is performed to probe the electron transfer studies between aqueous solution and gold nanorods (Au NRs). The seed-mediated growth method is used to synthesize crystalline cylindrical Au NRs having longitudinal plasmon resonance peak maximum at 825 nm. The as-synthesized Au NRs show average width and length of ~10 \pm 2 and ~50 \pm 2 nm, respectively, with an aspect ratio in the range of ~5. The time-resolved decay profiles have been studied in a subpicosecond resolution range using pump wavelength at 410 nm excitation and probe wavelengths from visible to near-infrared region. The plasmon dynamics studies of Au NRs depend on the electron heating phenomena, coherent acoustic phonon vibration and electronic transient behavior, i.e., electron-phonon coupling, and homogenous dephasing processes. Thus, the obtained results highlighted that the ultrafast charge transfer dynamics studies



in Au NRs could play an important role to elucidate their electronic, photothermal, and optical properties for molecular imaging, photothermal therapy, and optoelectronic and light-harvesting devices.

INTRODUCTION

Surface plasmon resonances (SPR) of gold nanorods (Au NRs) are induced by an incident electromagnetic excitation; collective and coherent oscillations occur in electrons presented in their conduction band.¹ The SPRs can lead to enhancement and confinement in large local field, which increases the light–matter interaction between the medium at nanometer range.^{2–4} The length and width of Au NRs in SPR modes correspond to the longitudinal and transverse excitations, respectively, which occur in the higher- and lower-wavelength regions of the absorption spectrum. The longitudinal SPR depends on various factors such as the surfactant materials, size, shape, and alignment of Au NRs.^{5–8}

The optical excitation perturbs the electronic distribution of nanoparticles/nanorods in the SPR band or interband as well as intraband transitions. The SPR band absorption changes due to the electronic distribution and lattice heating/cooling mechanism.^{9,10} Moreover, the internal electronic thermalization process and the scattering between the electron– phonon and phonon–phonon play a major role in describing the relaxation process in Au NRs.⁹ The electron dynamics as well as the relaxation process have been explored by ultrafast optical excitation at the surface plasmon resonance and away from it with the transient absorption spectroscopy (TAS).^{9–11} Basically, TAS is the time-resolved pump–probe method where the electrons in metal nanostructures are excited by a femtosecond pump pulse. The underlying mechanism is that the laser excited by a near-UV or visible pump pulse process

gives relaxation times under different frequency. The electron– phonon scattering (within 1–5 ps) thermalizes the hot electrons with its lattice so the broadening and bleaching phenomena occur between the plasmon resonance absorption bands. Further, the phonon–phonon scattering (within longer time scales of >100 ps) releases heat to the surrounding medium.^{11–15} The decay time of electron–phonon relaxation depends on the increased electron temperature, which is related to the power of the pump pulse that linearly rises with pump energy.¹⁶ Thus, the nanoscale thermal transport mechanism of Au NRs excited by pulsed laser serves as a promising multifunctional agent for biomedical imaging, photothermal therapy, and drug delivery. The few experimental studies have been focused on the electron dynamics of the Au NRs by pump–probe transient absorption spectroscopy.^{9–11,17–20}

Herein, the ultrafast dynamics studies of Au NRs synthesized by seed-mediated method are demonstrated. Basically, TAS analysis and femtosecond time-resolved studies using the pump-probe method around the surface plasmon resonance of Au NRs have been performed to interrogate the material response at an ultrafast time scale. For TAS measurements, both probe and pump are tuned in the visible wavelength range to excite the electrons for optimization of the absorption

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signals and avoiding any kind of error and artifacts. Additionally, the femtosecond laser provides major advantage of thermal confinement, which leads to sufficient time resolution for studying the co-relation between the distribution of excited electrons and phonon in Au NRs. Thus, Au NRs act as best legitimate to study the thermal transport behavior across the Au NRs along with the surroundings as well as in an aqueous medium.

RESULTS AND DISCUSSION

Prior to ultrafast studies of Au NRs, the structural/microstructural characterizations and spectroscopic studies are performed to detect the morphological, structural, and optical properties of Au NRs. Figure 1a,b shows the transmission



Figure 1. (a) TEM image, (b) HRTEM image (inset: magnified view), (c) SAED pattern, and (d) UV-vis spectrum of the assynthesized gold nanorods (inset: optical image of gold nanorods solution).

electron micrography (TEM) and high-resolution TEM (HRTEM) images of Au NRs, respectively. The obtained results reveal that the uniform and monodispersed Au NRs have width and length of $\sim 10 \pm 2$ and $\sim 50 \pm 2$ nm, respectively, with an aspect ratio in the range of ~ 5 . The TEM images at different places of sample are also shown in Figure S1 (see the Supporting Information). It confirms the synthesis of uniformly aligned gold nanorods having the same aspect ratio. The magnified view of the HRTEM image is displayed in the inset of Figure 1b. It exhibits the lattice fringes with *d* spacing of 0.148 nm with respect to the (220) plane of Au NRs.

crystallographic structure of Au NRs was also determined by selected area electron diffraction (SAED) pattern, as shown in Figure 1c, which also supports the HRTEM result. Further, UV-vis absorption spectrum of Au NRs colloidal solution is shown in Figure 1d, which reveals two absorption peaks: 530 and 825 nm. The peak in the shorter-wavelength region at 530 nm corresponds to the oscillation of plasmon in transverse mode, whereas the peak in the longer-wavelength region at 825 nm corresponds to oscillation of plasmon in the longitudinal mode. The absorption peak at 530 nm relates to spherical nanostructures, and the peak in the region 700-1300 nm relates to rod nanostructures of gold depending upon the aspect ratio of nanorods and seed concentration during the synthesis process.^{21,22} The obtained longitudinal peak wavelength value corresponds to ~ 5 nm aspect ratio, which has been calculated by generative adversarial networks theory²³ and discrete dipole approximation theory,^{23,24} clearly matching with TEM analysis. The optical image of the as-synthesized Au NRs colloidal solution is shown in the inset of Figure 1d, which displays wine red color under daylight. Furthermore, Figure S2 shows that the chemical stability of the as-synthesized Au NRs was also confirmed by performing UV-visible spectrum timeto-time in several statistical runs (see the Supporting Information). The obtained spectra show no change in the absorption peaks even after 7 days and 1 month, which confirms the chemical stability of Au NRs.

The chemical purity and elemental analysis of the Au NRs has been carried out via X-ray photoelectron spectroscopy (XPS). Figure S3a displays the XPS survey scan spectrum of Au NRs (see the Supporting Information). The binding energy in XPS result indicates the presence of carbon, oxygen, bromide, and gold elements. No other impurity elements were found. The high-resolution spectra of Au show doublet peak at 83.38 and 87.13 eV, corresponding to the presence of Au $4f_{7/2}$ and $4f_{5/2}$ states (Figure S3b; see the Supporting Information). The high-resolution spectra peak at 284.83 eV corresponds to C 1s carbon peak. It may be due to the cetyltrimethylammonium bromide (CTAB) that is present on the surface of Au NRs (Figure S3c; see the Supporting Information). The Ag(I) oxidation state is confirmed by the peak at 402.29 eV, which indicates the presence of Ag 3d states. The binding energy of Br 3d state is depicted by the peak at 68.46 eV, which is due to the presence of bromide in CTAB rather than silver bromide solution. Br/Ag ratio in the XPS images is in good agreement with the ratio present in CTAB.

The photoluminescence (PL) emission spectrum of the assynthesized Au NRs under 375 nm excitation wavelength is



Figure 2. (a) PL emission spectrum and (b) PL mapping image of as-synthesized gold nanorods; the inset shows the enlarged view of bundle of gold nanorods, which is systematically aligned in horizontal path.

shown in Figure 2a. Basically, the origin of PL is associated with three major reasons: (i) excitation of electron-hole pair, (ii) scattering in metals during relaxation of excited electron and hole on new states of energy, and (iii) finally, electronhole recombination.²⁵ In the present case, the localized d electrons (act as donor) are excited on the gold surface, and simultaneously holes (act as acceptor) are created due to the trapped energy associated on the surface states of Au NRs. Moreover, this recombination occurs between the electrons and holes present near to Fermi surface and in d band, respectively. The emissions are observed at 609 and 510 nm wavelengths for the regions of the X and L symmetry points, respectively, in first BZ. These observed peaks correspond to electron-hole recombination near X and L symmetry points, and the ratio of intensity of these peaks (I_x/I_I) is ~0.3. Electromagnetic local density of states (LDOS) is exposed by this spectral intensity of the nanorods, and the LDOS is associated with SP modes (eigenfunctions) in nanorods due to difference in plasmon mode excitation.²⁵ The as-synthesized Au NRs were also characterized by performing fluorescence PL mapping imaging; Figure 2b shows the luminescent signature of Au NRs and the inset shows the enlarged view of bundle of gold nanorods, which is systematically aligned in horizontal path. The PL mapping image and the associated PL emission spectra (excitation wavelength at 375 nm) of Au NRs are shown in Figure S4a,b (see the Supporting Information). These spectra are taken at different places of PL mapping image.

The TAS and dynamics studies of electron in plasmon modes for Au NRs have been performed by ultrafast spectroscopy. The low-energy pump fluences were used for avoiding the undesirable thermal effects in the aqueous medium. In TAS experiment, a pump beam excites the electrons so that the plasmonic oscillations occur and their subsequent dynamics changes have been investigated by timedelayed probe beam. These studies have been performed in the visible pump pulses centered at wavelength 410 nm and visible and near-infrared (NIR) probe pulses and fixed pump pulse energy at 0.35 mW. The TA spectra with varying delay times, 0-125 ps, in visible wavelength probe pulses are shown in Figure 3a. The visible light pumping excites the gold solution, and the bleaching effect occurs due to the excitation of



Figure 3. (a) Transient absorption spectra of gold nanorods solution under 410 nm excitation wavelength for different delay times, 0 s to 125 ps. (b) Transient kinetics decay spectra traces at 480, 538, 596, 687, and 758 nm and (c) their corresponding fitting curves for gold nanorods solution (visible pump pulses at 410 nm wavelength; visible light probe pulse and fixed pump pulse energy, 0.35 mW).

electrons into the conduction band, i.e., interband transition. This pumping effect increases the electron temperature due to moments of electrons in the gold nanostructures. These coherent oscillations correspond to acoustic vibrations of the nanorods.^{9–11} The bleaching peak intensity rises from 0 to 750 fs and then it reduces from 1.01 to 125 ps. It means that electrons and holes are accumulated for 750 fs time period in the conduction band. This enhances the plasmon band and transient bleaching state at a band maximum 540 nm in negative signal, whereas positive absorption arises centered at 490 and 580 nm. The bleaching peak wavelengths are shifted to the longer-wavelength side with increment in delay time. It means that the length of the Au NRs is increased due to lattice heating. The acoustic phonon vibrations occur due to the oscillations in bleaching peaks, which result in the increase of electron temperature, thereby also changing the dielectric constant.9 In the present investigation, gold solution is excited under low wavelength (410 nm) and the absorbed energy is divided into two modes (longitudinal surface plasmon resonance (LSPR) and transverse surface plasmon resonance (TSPR)). Further, initially, the bleaching in LSPR mode occurs under low excitation. After saturation of the LSPR mode, the absorbed energy will transfer to the TSPR mode, which increases the bleaching of the TSPR band.¹¹ Hence, the electron-phonon relaxation time corresponding to the TSPR mode is less compared to the LSPR mode under low excitation, which is strongly correlated with bleaching amplitude. Basically, bleaching amplitude depends on the quantity of the redistributed energies. Thus, the TSPR mode absorbs a large amount of energy and leads to increase in bleaching signal with lower damping rate.

For time delay studies of the bleaching peaks, the visible transient kinetics spectra and their corresponding fitting curves of gold nanorods solution are shown in Figure 3b,c. The polarity is positive near zero delay, i.e., $E_{\text{LSP}} < E_{\text{probe}}$. In comparison, $\Delta T/T$ is negative, $E_{LSP} > E_{probe}$, and photoinduced absorption occurs for the other wavelength. The interaction between transient photobleaching and photoinduced absorption with respect to the difference between $E_{LSP}-E_{probe}$ can be clearly stated by a model complex dielectric function $\varepsilon(\omega)$, which represents the contributions of free electrons (Drude part) and bound electrons (interband part). The decay curve clearly explains the plasmon-induced hot electron relaxation process, in which electron-electron scattering, fast electronphonon scattering, and slow phonon-phonon scattering take place.⁹ The decay time is calculated by the relaxation process of plasmon-induced hot electrons, i.e., the outcome from the heat exchange to the crystal lattice and then to the surrounding medium. Further, the time delay spectra are fitted by using biexponential decay function; their corresponding fitting components are given in the Supporting Information as Table ST1, which is of the order a few picoseconds, similarly to the earlier published results for Au NRs. The other research group also reported the TAS studies on Au NRs at 410 nm excitation wavelength and observed that the transient bleaching of TSPR and LSPR absorptions show similar intensity results to previous studies.^{9–11,17}

Figure 4a shows the TA spectra for NIR wavelength with varying delay times of 0-5.49 ns. The NIR wavelength light pumping excites the gold solution. The oscillations occur in the bleaching peaks with time. The bleaching peak intensity rises from 0 to 747 fs, and then it reduces from 1.02 to 5.49 ns. This enhances the plasmon band, and transient bleaching state



Figure 4. (a) Transient absorption spectra of gold nanorods solution under 410 nm excitation wavelength for different delay times, 0 s to 5.49 ns. (b) Transient kinetics decay spectra traces at 839, 918, and 1134 nm and (c) their corresponding fitting curves for gold nanorods solution (visible pump pulses at 410 nm wavelength; NIR light probe pulse and fixed pump pulse energy, 0.35 mW).

appears at band maximum 918 nm in positive absorption signal. The bleaching peak wavelengths are shifted to the lower-wavelength side with increment in delay time, which may be due to hot electron pressure and expansion in TSPR mode. These coherent oscillations correspond to acoustic phonon vibrations in breathing mode of the Au nanorods.⁹⁻¹¹ Figure 4b,c shows the decay times for Au NRs calculated from the triexponential fitting curve, and the NIR transient kinetics spectra and their corresponding fitting curve for gold nanorods solution. Further, the time delay spectra are fitted by using triexponential decay function; their corresponding fitting components are given in the Supporting Information as Table ST2. Thus, this is the most popular method to determine the time constants of various electron-phonon relaxation processes after photoexcitation of SPR modes of Au NRs.

Furthermore, the analysis of the pump-probe data is basically associated with the optical properties of the nanorods, which are altered due to the thermal-induced heating from laser. The laser pulse is incident on the plasmon Au NRs. Then, the decay phenomenon occur instantaneously due to the absorption of energy, which increases the temperature of conduction electrons in the rods. These electrons transfer heat to the Au lattice, and then this lattice exchanges heat with its surroundings through electron-phonon scattering and phonon-phonon scattering.⁹ The heat capacity of the surroundings acts as a source for the electrons and phonons to reach the final state at room temperature. Therefore, this electron temperature increase leads to transfer of the electrons above the Fermi energy, $E_{\rm F'}$ increases the number of energy levels below $E_{\rm F}$ for interband and intraband transitions, and finally widens the Drude response.9 It is also well established that interband transition in gold nanorods occurs from the d band into s-p band above the Fermi level, after excitation with 410 nm pulse wavelength. $^{9-11}$ As an outcome of this, the generated localized d band holes and electrons from conduction band are recombined within the range of few tens of femtoseconds. Further, the TSPR and LSPR bands are excited at the same time due to the absorption of energy. The electrons transfer to the conduction band, which leads to transient absorption phenomenon. Hence, these results clearly show that TAS provides a deep explanation of the optical characteristics of the probed medium.

CONCLUSIONS

In summary, ultrafast time-resolved TAS studies are performed to know the dynamics of SPR band in Au NRs. The Au NRs are synthesized using a seed-mediated growth method, having average width and length of $\sim 10 \pm 2$ and $\sim 50 \pm 2$ nm, respectively. The Au NRs reveal a TSPR band in the visible region at 530 nm wavelength and an LSPR band in the NIR at 825 nm wavelength. The Au NRs are excited under 410 nm pump wavelength and probed with different visible and NIR wavelengths. The results explain the lifetime of electronphonon recombination and phonon-phonon scattering, which is in the order of picosecond for the Au NRs. The heating in Au NRs lattice and lattice phonon interactions occur in visible and NIR probes, which dominate the oscillations of bleaching peaks to the extensional and breathing mode of the coherent acoustic phonon vibration for Au NRs, respectively. Thus, these deep insights into the optical dynamic nature of nanorods via ultrafast studies prove them as a promising candidate for various applications, including optoelectronics, sensing, contrast-enhanced imaging, and cancer therapeutics.

MATERIALS AND METHOD

Materials. Chloroauric acid (HAuCl₄·4H₂O, 99.99%), silver nitrate (AgNO₃, 99.8%), L-ascorbic acid (99.7%), hydrochloric acid (HCl, 36–38%), sodium borohydride (NaBH₄, 98%), sodium oleate (NaOL, >97%), and hexadecyl-trimethylammonium bromide (CTAB, 99%) were purchased from Sigma-Aldrich (St. Louis). Deionized water (DI) water (resistivity, 18.2 M Ω cm) was used as the solvent medium throughout the experiment.

Synthesis of Gold Nanorods. The crystalline cylindrical gold nanorods (Au NRs) with LSPR band peak maximum at 825 nm have been synthesized using a seed-mediated growth method. For particular aspect ratio of nanorods, the synthesis depends on various factors such as the quantity and size of seed particles, as well as pH and concentration of the solution. First, for the preparation of seed solution, HAuCl₄ solution (5.0 mL, 0.5 mM) was added into aqueous solution of CTAB (5.0 mL, 0.2 M) with continuous stirring at room temperature. Subsequently, a freshly prepared, ice-cold NaBH₄ aqueous solution (1.0 mL, 6.0 mM) was then immediately added into the mixture under vigorous stirring. Then, the prepared seed solution was stirred for 1-2 min and then left undisturbed at room temperature for 2 h. The change in color of the seed solution from yellow to brownish yellow indicates the formation of Au nanoparticles with diameters ranging between 5 and 8 nm. Further, for growth solution, CTAB (7.2 g) and NaOL (1.2 g) were dissolved in 250 mL of DI water. Then, the solution was cooled at room temperature and AgNO₃ solution (18 mL, 4.0 mM) was mixed. The mixture was kept undisturbed for 15 min, followed by the addition of HAuCl₄ solution (250 mL, 1.0 mM). The solution became colorless after 100 min of magnetic stirring. A certain amount of HCl aqueous solution was added into the solution. After another 15 min of slow magnetic stirring, the freshly prepared L-ascorbic acid solution (1.25 mL, 64 mM) is mixed to reduce Au(III) to Au(I). Finally, after 2 min of stirring, 0.8 mL of the Au seed solution was added into the obtained growth solution. Afterward, this mixed solution was vigorously stirred for few more seconds and then the resulting solution was placed under room temperature without disturbance for 12 h. After completion of the growth process, the prepared Au NRs

were centrifuged at high speed for 30 min to remove the supernatant, and this process was repeated two times to remove the excess of supernatant. Finally, the obtained precipitate was redispersed in DI water for further characterization.

Characterization. Transmission electron micrography (TEM) was performed (JEOL JEM 200 CX model operated at 200 kV) to determine the structure and aspect ratio of the as-synthesized Au NRs. A high-resolution UV-vis spectrophotometer (MODEL No. LS 55) was used to measure UV-visible spectra. XPS analysis was carried out in an ultrahigh vacuum chamber equipped with a hemispherical electron energy analyzer (PerkinElmer, PHI1257) using nonmonochromatized Al K α source. The photoluminescence (PL) and PL mapping were studied by WITec α 300R+ Confocal PL microscope system (WITec GnBH, Ulm, Germeny).

Ultrafast Transient Absorption (TA) Spectroscopy. To study the electron dynamics behavior in Au NRs, TA measurements were performed by femtosecond spectroscopy using pump-probe configuration. The system comprises a cavity-dumped Ti:sapphire oscillator (Micra from Coherent), Ti:sapphire amplifier (Legend from Coherent), optical parametric amplifier (OPA from Light Conversion), and spectroscopy system (Helios from Ultrafast Systems). Briefly, Ti:sapphire oscillator is used to generate 4 mJ (1 kHz) energy, \sim 35 fs pulse width centered at a wavelength of 800 nm. The output pulse was divided into two beams using a beam splitter, where one part of the 800 nm beam acted as the pump beam that goes through OPA to produce the 410 nm pump beam. Another part of the 800 nm beam was fed to a spectrometer to produce a wide-band white-light continuum probe pulse by passing through a combination of sapphire and CaF₂ crystals. Finally, the OPA output generates a highly stable beam of 410 nm wavelength, selected as a pump beam, and pump energy is fixed at about 0.35 mW. The data observed from the experiments were analyzed using Surface Xplorer software.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsome-ga.9b01157.

TEM imaging; UV spectra; XPS images; and PL spectra and PL mapping images (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kedawat08@gmail.com (G.K.). *E-mail: bipinbhu@yahoo.com (B.K.G.).

ORCID 0

Govind Gupta: 0000-0001-5006-7623 Bipin Kumar Gupta: 0000-0002-0176-0007

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

Au NRs, gold nanorods; SPR, surface plasmon resonance; TAS, transient absorption spectroscopy; LDOS, local density of states; TSPR, transverse surface plasmon resonance; LSPR, longitudinal surface plasmon resonance

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