Femtosecond transient absorption dynamics of close-packed gold nanocrystal monolayer arrays

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Abstract

Femtosecond transient absorption spectroscopy is used to investigate hot electron dynamics of close-packed 6 nm gold nanocrystal monolayers. Morphology changes of the monolayer caused by the laser pump pulse are monitored by transmission electron microscopy. At low pump power, the monolayer maintains its structural integrity. Hot electrons induced by the pump pulse decay through electron–phonon (e–ph) coupling inside the nanocrystals with a decay constant that is similar to the value for bulk films. At high pump power, irreversible particle aggregation and sintering occur in the nanocrystal monolayer, which cause damping and peak shifting of the transient bleach signal.

1. Introduction

Hot electron relaxation dynamics in nanoparticles has been an active research area because it can reveal the change of electronic and lattice vibrational properties when the size of materials approaches the nanometer scale [1–9]. Time-resolved femtosecond spectroscopy is the primary technique used to investigate these fast relaxation dynamics. The principle of this technique is to excite electrons to higher energy levels through a short pump laser pulse. The excited nonthermalized electron distribution quickly relaxes on a femtosecond time scale into a Fermi–Dirac distribution with a higher electron temperature through electron–electron (e–e) interaction. The thermalized hot electron distribution then cools down through electron–phonon (e–ph) coupling, and eventually dissipates the excess energy through phonon–phonon (ph–ph) coupling, either within the nanoparticle or into the surrounding environment. The relaxation process can be monitored by measuring the transient absorption spectrum though a probe laser pulse that is variably delayed from the pump pulse. The change of electronic distribution will cause a change of the dielectric constant, which affects the transient absorption of the probe pulse. Most of the pump–probe experiments carried out so far use either diluted metal nanoparticle colloids, or nanoparticles embedded in a dielectric matrix [1–12]. Aside from the potential problem of large particle size distribution in these experiments, the optical density of these samples is typically quite low, and varies from one experiment to another. These issues have complicated the elucidation of the size range the e–ph coupling constant would deviate from its bulk value. Because of the finite particle size, the transient absorption decay caused by e–ph coupling can be entangled with ph–ph coupling, especially with high

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energy pump pulses. The increase of the e–ph coupling constant with pump power [10] could depend on the details of ph–ph coupling in the nanocrystals as well as the coupling to their environment [11]. Therefore, the true e–ph coupling constant, which reveals the change of intrinsic electronic and vibrational states due to finite size, can only be probed at low pump power when the contribution from ph–ph coupling is relatively weak. The low optical density in various samples creates a challenge to obtain high signal-to-noise ratios for measurements using low pump power. Furthermore, the effect of the pump pulse on the sample structure, and how that would affect the transient dynamics is not well understood, because effort has been made to study the change of sample morphology after the pump–probe experiments [13,14]. In this work, we study transient absorption spectra and kinetics of a self-assembled close-packed nanocrystal monolayer consisting of monodispersed nanocrystals. The highly uniform particle size reduces the effect of inhomogeneous broadening. The close-packed nature of the monolayer increases the optical density significantly that, in turn, allows low pump power measurements to be carried out on these samples with high signal-to-noise ratio. We also monitored the sample morphology after the pump–probe experiments by transmission electron microscopy (TEM), which allows us to study the effect of the laser pulse on the sample structure.

2. Experimental

Gold nanocrystals were synthesized according to a procedure previously developed by one of us [15]. Our synthesis is a single-phase reaction in an organic solvent containing cationic surfactant. The as-prepared nanocrystals were then coated with dodecanethiol through ligand exchange. We have also shown that by adopting a digestive ripening process in an environment of excess thiol, the particle size distribution can be greatly narrowed. Further size segregation caused by lowering the colloidal temperature can produce highly monodispersed nanocrystals of roughly 6 nm in diameter (with standard deviation of particle size <5%).

The formation of nanocrystals into a 2D monolayer is influenced by a variety of experimental parameters. Particle size affects the strength of interparticle van der Waals interaction. If the interparticle attraction energy was larger than the thermal energy, the formation of 3D nanocrystal superlattices would occur in the solution phase before they are deposited on the surface. For 6 nm gold nanocrystals in toluene ligated with dodecanethiol, dynamic light scattering experiments have shown that particles can remain as single particles when the density of particles remains lower than the critical concentration [16]. Through evaporating a droplet of nanocrystal colloid on a substrate, a monolayer of nanocrystal film can be formed. It has been recently shown through in situ small angle X-ray scattering experiments that the formation of a 2D nanocrystal array occurs at the liquid–air interface when the initial evaporation rate is fast enough that the density of particles becomes saturated near the interface [17]. By adopting this technique, we can form a monolayer with either short range order or long range order depending on whether there is enough dodecanethiol ligand coating on the nanocrystal surface [18]. The samples used for pump–probe experiments are made with colloids that have been precipitated several times and contain a minimum concentration of thiol, thus forming 2D monolayers with short-range order on the substrates.

The substrates were silicon nitride membranes (100 nm thick), formed on silicon substrate (3 × 4 mm²). The silicon wafers were patterned with photolithography and are chemically etched from the backside to open a window area of 200 × 200 μm² with a free-standing silicon nitride membrane [19]. Nanocrystals were then self-assembled on these substrates, which allowed pump–probe measurements as well as TEM to be performed on the same sample area through the silicon nitride membrane window.

The laser system has been described in detail elsewhere [20]. Briefly, a regeneratively amplified Ti:sapphire laser produces 130 fs pulses at 1 kHz, with a pulse energy of 400 μJ/pulse and a center wavelength of 835 nm. This output is split into two beams. One is used to generate the white light continuum ‘probe’ pulse by focusing into a 1 mm sapphire window. For these experiments, transient spectra utilized the portion of the continuum extending from 450 to 750 nm. The other beam is frequency doubled to 417 nm and serves as the ‘pump’ pulse. The probe pulse is variably delayed on an optical delay line in order to obtain the transient spectra or kinetics. The spectra were collected in a chirp free manner by moving the probe delay line by an amount equal to the measured chirp.

3. Results and discussion

A typical transient absorption spectrum of the monolayer at its maximum signal is shown in Fig. 1, with 100 nJ pump pulses. There is an increase of absorption in both the short wavelength region (450–480 nm) as well as the long wavelength region (>600 nm). Also, is a negative transient absorption (bleaching) at the same wavelength as the ground state plasmon absorption peak is observed. These transient features reflect the change of electron distribution induced by the femtosecond pump pulse, which in turn cause a significant change of nanocrystal dielectric constant [21], as well as a possible enhancement of e–e scattering rate [8], both
will cause a broadening of plasmon absorption. The recovery of the plasmon bleach reflects the energy dissipation of hot electrons created by the pump laser pulse. At low pump power, this decay process is through e–ph coupling only. The inset of Fig. 1 shows the experimental bleach recovery data, which can be fit by a single exponential decay curve. The decay time constant is 1.0 ps. The fact that this e–ph decay time constant is close to the value in bulk gold films [22,23] indicates that for 6 nm gold nanocrystals, both the electronic and phonon spectra are close to the bulk value, and quantum size effects and surface phonon mode scattering are negligible. This is in agreement with the recent experiments by Link et al. [24], Hodak et al. [5] and Arbouet et al. [25].

In order to probe the effect of coupling between hot electrons and surface phonon modes, higher energy laser pump pulses must be used. TEM images of the samples after high energy pump–probe experiments reveal that the laser pulse can cause significant structural changes in the monolayer. The extent of the change depends on both the pump power and the length of time that the sample is exposed to the laser beam. Fig. 2a shows a typical monolayer of nanocrystals before the pump–probe experiments. Nanocrystals are arranged in a hexagonal lattice due to the interplay of van der Waals attractions between nanocrystals and the steric repulsion due to interdigitation of the surface ligands. Fig. 2b shows the sample after pump–probe experiments using 150 nJ pump pulses. The majority of particles have shifted away from their hexagonal lattice positions. A further increase of pump energy to 300 nJ causes a significant amount of sintering among particles (Fig. 2c). This structural change of the monolayer is directly reflected in the pump–probe data. Fig. 3 shows three
consecutive measurements of the maximum bleach spectra at 300 nJ pump pulse energy. The bleach signal gradually decreases and the bleach peak shifts about 10 nm towards the red. This shift of the bleach maximum indicates the corresponding ground state plasmon absorption peak also shifts towards longer wavelength. It is well-known from previous experiments and theoretical modelling that the coupling between nanocrystals will shift the plasmon absorption towards longer wavelength [12,26]. The decrease of bleach signal is a result of reduced absorption cross-section as particles in the monolayer start to overlap and sinter.

Laser pump pulse induced sample morphology changes have been reported in several experiments using colloidal solution samples [23,27] and in fractal-like nanocrystal thin films [13]. However, in those experiments, much higher pump pulse energies (μJ to mJ) were used, typically leading to fragmentation and shape change of individual particles due to thermal heating and melting of the individual nanocrystals. The fact that for a monolayer of nanocrystals, pump pulses with relatively low energies (~300 nJ) can change the morphology has not previously been realized to our knowledge. The formation of clusters of nanocrystals by pulsed laser irradiation (Fig. 2b) indicates that electrostatic dipolar interaction might play an important role in shifting particles away from their hexagonal lattice positions. Thermal heating eventually induces sintering of these overlapped clusters.

We can estimate the lattice temperature increase of the nanocrystal under the illumination of femtosecond pump pulse. Using the measured transmittance of the nanocrystal film (0.89), particle density (3.6 x 10^4 μm^-2), laser spot diameter of 100 μm, and heat capacity of bulk gold (129 J/kg K), the lattice temperature increase of the gold nanocrystal is ~130 K for 100 nJ pulses and ~390 K for 300 nJ pulses. Even with the 300 nJ pulse, the increase of temperature is not sufficient for direct melting of nanocrystals (~840 °C for 6 nm particles) [28]. However, it is sufficient to induce sintering of nanocrystals when they are in close proximity. The desorption of dodecanethiol ligand at this temperature might also be possible [29]. Differential scanning calorimetry measurements of similar size gold nanocrystals aggregates (3D) have shown a strong exothermic peak at 220 °C [30], which is caused by particle sintering and subsequent releasing of surface energy. To achieve this lattice temperature, the pump pulse energy needs to be 150 nJ, which corresponds well with the experimentally observed threshold pump pulse energy that start to induce significant sintering (Fig. 2b).

The robustness of the nanocrystal monolayer can be improved by exposing the monolayer to an electron beam. We have previously shown that electron beam lithography can be used to pattern arbitrary two dimensional areas of nanocrystals on the substrate from an extended monolayer [31]. In this technique, high dosage electron beam can cause the C–H and C–C bond of the ligand to break, which could create a carbonaceous film to bind the nanocrystals to the substrate [32]. TEM has shown that the monolayer structure remains intact during the e-beam exposure. This same technique can be used to improve the stability of the monolayer under femtosecond pump pulse excitation. Fig. 4 shows a series of maximum bleach curves for an e-beam-written monolayer (exposed a 30 keV electron beam at 30 pA, at a dose of 7200 μC/cm^2) and a reference monolayer prepared under the identical condition but without exposure to the electron beam. Both samples were then exposed to 100 nJ pump pulses, followed by 300 nJ pump pulses and finally 100 nJ pump pulses. The exposure time to different energy pump pulses was kept approximately the same for both samples. For the e-beam written sample, after the 300 nJ pump exposure, the maximum bleach signal at the second 100 nJ exposure remains almost the same as the first exposure, whereas for the reference sample, the bleaching signal becomes significantly reduced. This indicates e-beam exposure can prevent sample aggregation and sintering caused by the femtosecond pump pulse. Detailed

Fig. 4. Comparison of maximum transient absorption between e-beam exposed sample (a) and reference sample (b). Each sample had consecutive scans exposed to 100, 300, and 100 nJ pump pulse energies at 417 nm. Dashed lines are aides to the eye.
comparison between these two samples also shows that the morphology change under the pump pulse will cause the overall width of the transient bleach band to become broader and nonsymmetric with respect to its peak (Fig. 4b). This is an indication that particle aggregation under pump pulse illumination causes the nanocrystal monolayer to become inhomogeneous. Aggregated or sintered particles cause the ground state plasmon absorption peak to shift toward longer wavelength. Consequently, the transient absorption spectra acquire a long wavelength tail. TEM experiments after the pump–probe experiments confirm that the majority of particles remain in the hexagonal position for the e-beam written sample, whereas the morphology of reference sample is close to Fig. 2c. For the e-beam written sample, further increase of the pump power above 500 nJ still causes some degree of aggregation. The robustness of the monolayer must continue to be improved to permit more detailed experiments on ph–ph coupling across the particle surface.

4. Conclusion

We have performed the first femtosecond pump–probe experiments on gold nanocrystal monolayers that are self-assembled on a silicon nitride membrane widow. TEM through the membrane window allows us to correlate the change of the pump–probe transient absorption signal with the change of sample morphology. We found that, for low laser pump power (~100 nJ pulse), the nanocrystal monolayer maintains its structural integrity, and the e–ph coupling constant for 6 nm diameter particles is close to that for bulk films. This indicates the intrinsic electronic and vibrational modes of the 6 nm particles are similar to the bulk. However, at higher pump pulse energy (>150 nJ), the interaction between pump pulse and sample causes the particles to shift away from their lattice positions and ultimately sinter with the neighboring particles. The structural change of the sample causes signal damping and a red shift of the transient absorption bleach during the aggregation process. This can be explained qualitatively by a change of the ground state absorption of the monolayer as a result of particle aggregation. We demonstrated that exposure of the monolayer to an electron beam can increase the threshold where the irreversible morphology change of the monolayer.

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