4C15　銀ナノ微粒子の構造とダイナミクスのフェムト秒レーザー分光による研究

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【Purpose】Nanoparticles have a variety of unique spectroscopic, electronic, and chemical properties that arise from their small sizes and high surface/volume ratios[1]. In particular, noble metal clusters and colloids with nanometer dimensions have attracted a great deal of interest recently. The quantum size effect, nonlinear optical effect, and electron dynamics of noble metal nanoparticles are being extensively investigated, because they can be applied in catalysts, sensors, drug delivery, optoelectroelectric, and magnetic devices.

【Experimental】We have prepared three kinds of Ag colloidal nanoparticles: (1) dodecanethiol-derivatized Ag nanoparticle (sample-1), pure Ag nanoparticles dissolved in water (sample-2), and long-chain carboxylate acid protected Ag nanoparticles (sample-3), respectively. Sample-1 is prepared by using two-phase liquid-liquid system[2]. Sample-2 is synthesized by the direct adding of reduction agent ($NaBH_4$) to the precursor solution of $AgNO_3$. Sample-3 is made by solvent free preparation method with treating the mole ratio (1:10) of silver actate and oleic acid at 150°C-1h. The excited-state dynamics of samples are studied by using femtosecond laser spectroscopy and picosecond single-photon timing spectroscopy. The average particles of samples are preformed by the TEM observation. The photoexcitation in the interband leads to the heating of conduction electron gas and its subsequent thermalization through electron-electron and electron-phonon interaction. The results are compared to the dynamics of Ag nanoparticles with changing the laser intensity and solvent effects.

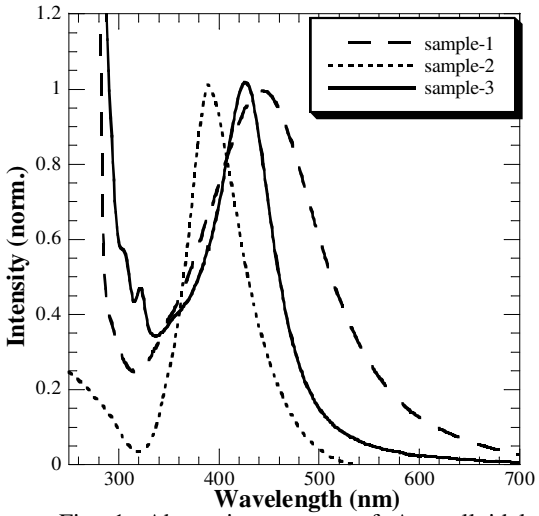

Fig. 1. Absorption spectra of Ag colloidal nanoparticles for sample-1, 2, and 3, respectively.

【Results and Discussion】The absorption spectra of samples are shown in Fig. 1. The surface plasmon peaks of sample-1, 2, and 3 are observed at about 440, 390, and 420 nm, respectively. The difference peak position can be considered on the change in refractive index of surrounding mediums. The TEM observation revealed that homogeneous dispersion and the average particle size of samples are 4~10 nm, respectively.

Optical excitation into the plasmon band creates hot electrons as manifested by bleaching of this band. The bleach recovery can be described by a biexponential. The first component with a decay time between about 1 and 10 ps is attributed to electronic energy relaxation through electron-phonon coupling. The second component with a decay time of several tens of picoseconds originates from the subsequent cooling of the lattice by phonon-solvent interaction[3].

The transient absorption spectra and their temporal profiles for sample-1, 2, and 3 are shown in Fig. 2,

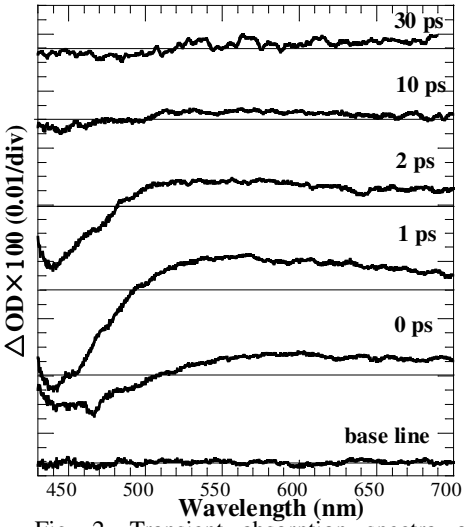

Fig. 2. Transient absorption spectra of sample-1 dissolved in toluene at different time delay, λ_{ex}=390 nm.

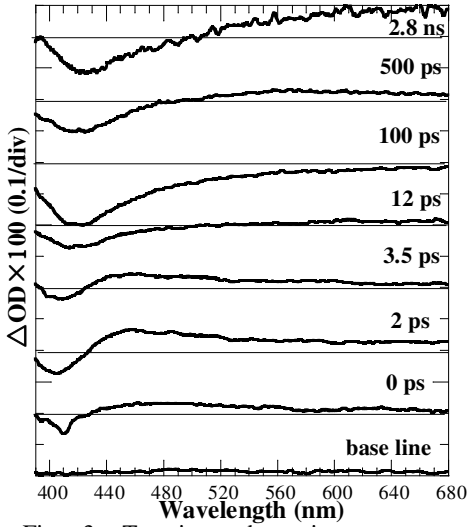

Fig. 3. Transient absorption spectra of sample-2 dissolved in water at different time delay, λ_{ex}=360 nm.

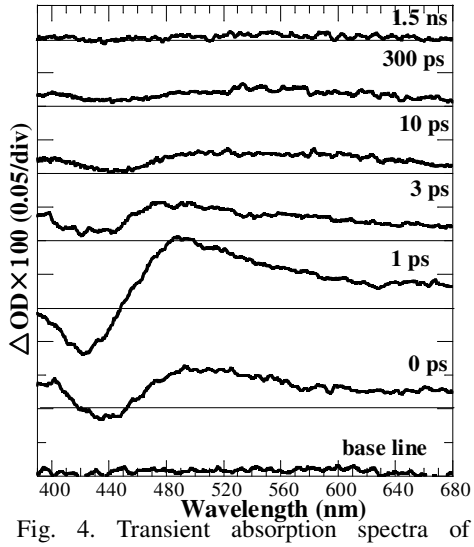

Fig. 4. Transient absorption spectra of sample-3 dissolved in toluene at different time delay, λ_{ex}=360 nm.

3, and 4, respectively. The strong bleaching (around 410~440 nm) and a positive transient absorption above 480 nm are observed. For sample-1, the bleaching peaks are recovered within a few picosecond time scales. The positive absorption peak exists until a few hundred picosecond time scales. In the case of sample-2, the bleaching peaks become weak in a few ten picosecond and than strong bleaching peak with large width appear again. This peak is shifted to longer wavelength. Both bleach and positive absorption remain until a few nanosecond time scales. For sample-3, the bleaching peaks are recovered within a few picosecond time scales. The positive absorption peak remains until a few hundred picosecond time scales. This phenomenon is very similar to that of sample-1. From the results, the behavior of excited state dynamics of samples is different with and without capping (stabilizing) agent. Therefore, we tried to prepare sample-3 dissolved in various solvents (toluene, cyclohexane and NaOH solution) with different silver acetate/oleic acid molar ratios and examined their excited-state dynamics. It is clear that the phonon-phonon coupling time depends on the surrounding mediums. We will also report on the dependence of laser power intensity on the relaxation dynamics and luminescence of Ag nanoparticles.

【References】 (1) S. L. Longunov, T. S. Ahmadi, M. A. El-Sayed, J. T. Khoury and R. L. Whetten, *J. Phys. Chem. B*, 1997, 101, 3713. (2) M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc, Chem. Comm.,* 1994, 801. (3) T. W. Roberti, B. A. Smith, and J. Z. Zhang, *J. Chem. Phys.,* 1995, 102, 3860.