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# Ultrafast energy transfer of silver ultrafine particles in aqueous solutions as investigated by the ultrafast lensing effect technique

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## Abstract

Ultrafast relaxation dynamics of silver ultrafine particles in aqueous solutions was measured by an ultrafast lensing effect (ULE) method using two types of samples with SDS (sodium dodecyl sulfate) and without SDS. The fit to the ULE time evolution required three exponential components: one for the increase and two others for the decrease. The time constants were estimated as 1, 3, 7 ps for the sample without SDS and as 1, 2, and 23 ps for the sample with SDS. The ultrafast relaxation dynamics was discussed in connection with the behavior of photoexcited electrons. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Metallic ultrafine particles (1–100 nm in diameter) have received a growing attention because they exhibit anomalous physical properties which are not observed in bulk solid phases [1,2]. Among them, silver ultrafine particles have been exclusively investigated in connection with surface-enhanced Raman spectroscopy (SERS), nonlinear optical effect, quantum size effect, etc. The relaxation process in silver ultrafine particles after photo-excitation can be regarded as the fundamental process of these effects. Therefore, the observation of the ultrafast relaxation via energy transfer across the silver-solution inter-

face will provide great insight into the anomalous physical properties of the ultrafine particles. Moreover, the ultrafast energy transfer across the liquid/solid interface represents the most interesting and important processes in various fields of physical chemistry, biophysics and engineering because it is fundamental for understanding photocatalysis, electrode reaction, etc. In the present study we focus on the ultrafast energy transfer at the interface between the silver ultrafine particles and the aqueous solutions.

Based on the recent development of femtosecond pulsed-laser technologies, a number of ultrafast spectroscopic techniques have been developed and have provided information on ultrafast processes such as energy transfer and molecular dynamics [3–7]. Among them, transient absorption spectroscopy has

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been widely used to monitor the transient processes in solutions after excitation [3], but it cannot detect transient species with low concentration because of its low sensitivity. Fluorescence measurements using up-conversion techniques have been reported for various luminescence samples [5], but this technique cannot be applied to non-luminescent samples. An optical technique with high sensitivity and high applicability is highly desirable.

We have developed and reported on a number of photothermal spectroscopic techniques, which have advantages of sensitivity and applicability over the other spectroscopic methods [8–10]. After a preliminary trial to combine the same optical configuration as that adapted in a thermal lens method with an ultrafast pump–probe technique, we have developed a femtosecond ultrafast lensing effect (ULE) technique and have successfully investigated ultrafast nonradiative dynamics of all-*trans*- $\beta$ -carotene and Auramine O in dilute *n*-hexane solutions [11,12].

In this work, we performed ULE measurements of silver ultrafine particles in aqueous solutions. The aim of this work is to reveal the process of ultrafast energy transfer across the interface between silver ultrafine particles and aqueous solutions. We present the first measurements of the ultrafast relaxation of the excited silver ultrafine particles in aqueous solutions.

## 2. Experimental

### 2.1. Principle and apparatus

The principle and apparatus have been described in our previous Letter [11]. A brief outline follows here based on Fig. 1. The ULE method detects the ultrafast change in refractive index induced by a pump beam. In some cases, the change in the refractive index can occur before the light energy is transformed into heat. We term this an ‘ultrafast lensing effect (ULE)’. There are many possible physical origins of ULEs [13,14]. It should be noted that the present ULE signal change includes both the real and the imaginary components of the refractive index. Distinguishing between the real and the imaginary components will be possible by getting the ULE signals with various wavelengths and analyzing them

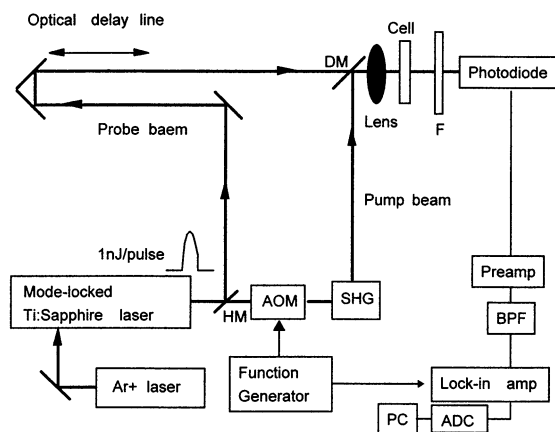


Fig. 1. Experimental setup for the ultrafast lensing effect method. AOM, acousto-optic modulator; DM, dichroic mirror; F, colored glass filter; SHG, second harmonic generator; HM, half mirror; BPF, band-pass filter; ADC, analog-to-digital converter; PC, personal computer. The other optical elements are mirrors.

with the Kramers–Kronig relation. This will be a next topic of our research.

The laser system consisted of a mode-locked Ti:sapphire laser (Coherent, Mira 900F) pumped by an Ar-ion laser (Coherent, Innova 310), which produced femtosecond optical pulses with a repetition rate of 76 MHz, centered at 780 nm. Each pulse had an energy of 1 nJ/pulse and 150 fs duration (FWHM) for the autocorrelation. The output beam was divided into two by a half mirror. One was used as a probe beam after passing it through a computer-controlled optical delay line. The other beam was frequency-doubled to generate a 390 nm pump beam after being intensity-modulated by an acousto-optic modulator at 1.4 MHz. The pump and probe beams were coupled with a dichroic mirror, focused by a convex lens ( $f = 50$  mm) and collinearly incident into the sample solution with a 0.5 mm optical path length. Polarization planes of the pump and probe beams were set both parallel and vertical to each other in order to examine the directionality of the energy transfer. The change in the divergence of the probe beam was detected as an intensity change at the center of the probe beam, which was measured with a small-area avalanche photodiode (0.1 mm  $\varnothing$ ). The photodiode output was passed through a pre-amplifier and a home-made passive band-pass filter before being fed into a lock-in amplifier (EG & G Princeton

Applied Research, Model 5202) used for sensitive phase detection.

The fluence of the pump beam was  $0.3 \text{ mJ/cm}^2$ , and the magnitude of the temperature change was estimated to be 70 K. These were chosen to avoid boiling of the solvent. The relative change in intensity at the detector was  $10^{-5}$ – $10^{-4}$ .

## 2.2. Sample preparation

A colloidal silver solution was prepared by reducing silver nitrate ( $\text{AgNO}_3$ ) by sodium borohydride ( $\text{NaBH}_4$ ) in water at  $0^\circ\text{C}$  [15]. The formation of ultrafine particles ( $\sim 10 \text{ nm}$ ) was confirmed by absorption spectra with a UV-visible spectrometer (JASCO, V-570). The concentration of the prepared solution was estimated to be ca.  $8 \times 10^{-9} \text{ M}$ . In order to investigate the effect of adsorbate to the energy transfer across solid/liquid interfaces, we measured two kinds of samples: colloidal silver solutions (1) without SDS (sodium dodecyl sulfate) and (2) with SDS. In case of preparation of the colloidal silver solution with SDS (2), SDS was added to  $\text{NaBH}_4$  aq (2 mM) in advance before reduction of  $\text{AgNO}_3$ . The concentration of SDS in this case was 1 mM. The SDS molecules are adsorbed at the surface of the ultrafine silver particles forming a monolayer with a thickness of ca. 20 nm and stabilize the colloidal silver solution.

## 3. Results and discussion

ULE signals of aqueous colloidal silver solutions with SDS and without SDS are shown in Fig. 2. For comparison, the signal for pure solvent (water) is also shown. The increase in the signal corresponds to the photo-induced increase in the refractive index of samples and vice versa. Around delay time zero, the signals show an abrupt rise over the baseline followed by an abrupt fall. After the initial sharp rise and fall, the signals increase again gradually beyond the baseline and subsequently decrease gradually toward the baseline.

The initial sharp rise and fall show a symmetric peak shape, which was fitted to a Gaussian shape with less than 400 fs of full-width at half maximum

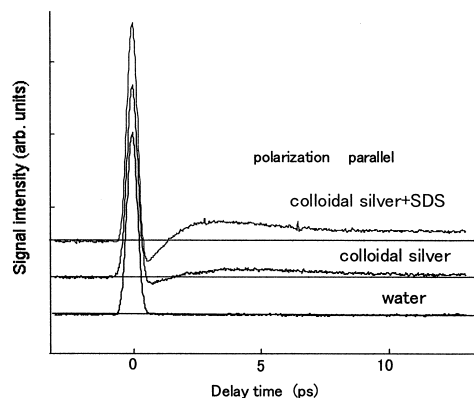


Fig. 2. The raw data of ULE signals for silver colloidal aqueous solutions. Baselines are shifted for good visibility.

(FWHM). Such a signal was also observed for the blank sample. As we reported previously, the initial sharp peak is attributable to the optical Kerr effect (OKE), a third nonlinear effect, of the solvent [11,12]. The OKE for the solvent increases the refractive index and the OKE temporal evolution follows a cross correlation between the pump and probe pulses because the electronic response time dominating the sharp signal is on the order of 1 or 10 fs faster than the pulse width ( $\sim 200 \text{ fs}$ ). Thus we regard the center of the initial sharp peak as delay time zero. The component around the OKE before the signal reached its minimum was neglected in the analysis of the ultrafast relaxation of ultrafine particles. Since the signals of the OKE diminished within several hundred femtoseconds, they had no influence on the time constants we determined for ultrafine silver particles.

The observed ULE signals were analyzed using a least-square fitting method. The curve was fitted with a summation of some exponential functions. A tri-exponential model was found to provide the best fitting with ULE signals. The curve  $I(t)$  is formalized as

$$I(t) = C_1 \exp(-t/\tau_1) + C_2 \exp(-t/\tau_2) + C_3 \exp(-t/\tau_3).$$

The first exponential function is for the primary gradual increase and the other two for the subsequent decrease. The time constants were estimated as 1, 3, and 7 ps for the colloidal silver solution without SDS

Table 1  
Results of multi-exponential fitting

Ag colloid	Polarization	Time constants (ps)			Pre-exponential factors		
		$\tau_1$	$\tau_2$	$\tau_3$	$C_1$	$C_2$	$C_3$
Without SDS	parallel	1	3	7	−1	−0.36	+0.65
	perpendicular				−1	+0.45	+0.12
With SDS	parallel	1	2	23	−1	+0.79	+0.06
	perpendicular				−1	+0.79	+0.08

and as 1, 2, 23 ps for the solution with SDS (Table 1). The comparison between the fitted curves and the experimental ones is shown in Figs. 3 and 4. Interestingly, the second component of the solution without SDS (2 ps) was dependent on the polarization plane, that is, the intensity of the second component changed by changing the polarization angles between the pump and probe beams from parallel to vertical. Although the second components ( $\tau_2$ ) for both samples with SDS and without SDS are in the same time region (2–3 ps), the corresponding phenomena are considered to be different from each other. This is because the sample without SDS exhibits a depen-

dence on polarization plane whereas that with SDS shows no dependence.

In the present case, it is considered that the refractive index change mainly reflects energy transfer dynamics from silver ultrafine particles to solvent molecules. Based on the previous report on the transient reflectivity measurement of silver thin film [16], we assigned  $\tau_1$  to the relaxation of photoexcited electrons in the particles for both cases with and without SDS. The following relaxations toward the baseline ( $\tau_2$ ,  $\tau_3$ ) are considered to reflect the energy transfer process from silver particles to solvent molecules.

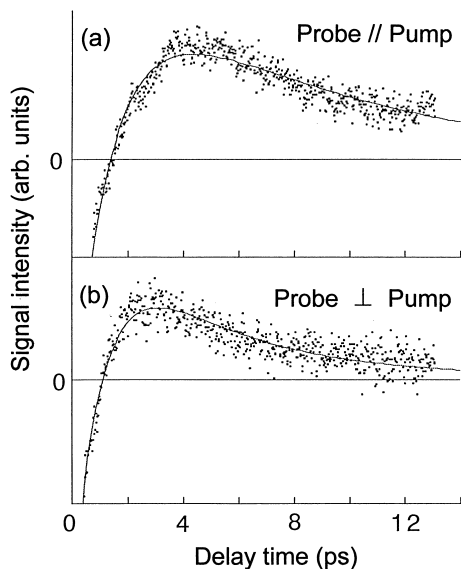


Fig. 3. Comparison between the obtained ULE signals (depicted by dots) for silver colloidal aqueous solutions without SDS and fitted curves (solid lines). The polarization planes of the pump and the probe beams are (a) parallel to each other and (b) perpendicular to each other.

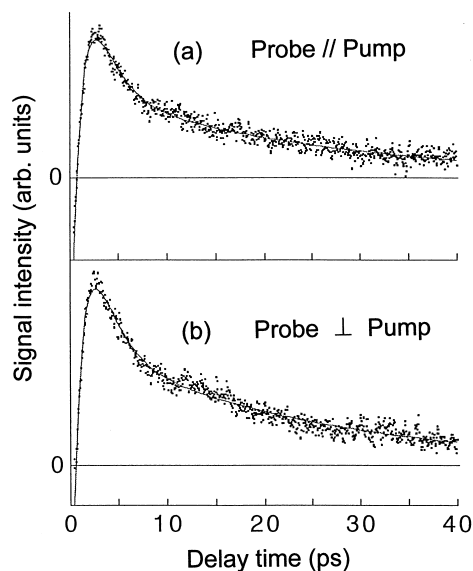


Fig. 4. Comparison between the obtained ULE signals (depicted by dots) for silver colloidal aqueous solutions with SDS and fitted curves (solid lines). The polarization planes of the pump and the probe beams are (a) parallel to each other and (b) perpendicular to each other.

Details can be added by analysis based on rate equations describing the energy stream. At first we assume conventional heat conduction processes in which the heat flux is simply proportional to the difference between the two bodies. In the ultrafast time region, the temperatures of the electrons and the phonons should be defined separately and each temperature is used instead of the bulk temperature. Thus, if the thermal conductivity or the time constants estimated from the following equations are inconsistent with the reported conventional values, the energy transfer process in the present system cannot be explained by a simple heat conduction. In such a case, the temperature of photoexcited electrons and novel energy transfer coefficient by them should be substituted into the equations.

Here we introduce the equations describing the conventional heat conduction. The particles act as heat resources, and heat conduction occurs from the particles to the solvent. The case with the SDS layer can be presented as follows. Thermal resistance exists at the interface between the particles and the SDS layer, and the SDS layer and the solvent. The rate equations describing this case are formalized as

$$Q(t) = Q_0 \exp(-k_1 t) \quad (1)$$

$$\rho_{\text{Ag}} C_{\text{Ag}} V_{\text{Ag}} \frac{dT_{\text{Ag}}(t)}{dt} = Q(t) - h_1 S_{\text{Ag}} [T_{\text{Ag}}(t) - T_{\text{SDS}}(t)] \quad (2)$$

$$\rho_{\text{SDS}} C_{\text{SDS}} V_{\text{SDS}} \frac{dT_{\text{SDS}}(t)}{dt} = h_1 S_{\text{Ag}} [T_{\text{Ag}}(t) - T_{\text{SDS}}(t)] - h_2 S_{\text{SDS}} T_{\text{SDS}}(t) \quad (3)$$

where  $Q_0$  is the energy given to the silver particle by light,  $k_1$  ( $= 1/\tau_1$ ) is the rate constant of deactivation of photoexcited electrons,  $\rho$  is the density,  $C$  is the specific heat,  $V$  is the volume,  $T$  is the temperature,  $S$  is the surface area, and  $h$  is the thermal conductivity.  $Q(t)$  corresponds to the heat quantity generated at the heat sources, i.e., silver particles. The temperature of the silver particles is determined by the heat generation by deactivation of photoexcited electrons in the particles and heat conduction from the silver particles to the SDS layer (Eq. (2)). Similarly, the temperature of the SDS layer is deter-

mined by the heat conduction from the silver particles and that toward the solvent matrix (Eq. (3)). Solving these equations,  $T_{\text{Ag}}(t)$  is obtained as the sum of tri-exponential functions.

The case without SDS layer can be presented by more simple equations.

$$Q(t) = Q_0 \exp(-k_1 t) \quad (4)$$

$$\rho_{\text{Ag}} C_{\text{Ag}} V_{\text{Ag}} \frac{dT_{\text{Ag}}(t)}{dt} = Q(t) - h_1 S_{\text{Ag}} [T_{\text{Ag}}(t) - T_{\text{sol}}(t)] \quad (5)$$

In this case,  $T_{\text{Ag}}(t)$  is obtained as the sum of bi-exponential functions. Thus, if we assume these equations, the ULE relaxation should have two components.

It can be considered that the above Eqs. (1)–(5) are consistent with our tri-exponential fitting results, except for the polarization dependent  $\tau_2$  of the sample without SDS. Thus, the experimental time constants from the fitting results can be interpreted as the time constants of each process in the above equations, except for  $\tau_2$  of the sample without SDS. Based on this interpretation, the observed ultrafast relaxations were discussed as follows.

First, we discuss the time constants of the colloidal silver particles without SDS. If we assume a conventional heat conduction from silver particles to solvent, the following equation can be applied to our experiment,

$$h = k/R \quad (6)$$

Here  $h$  is the heat conductivity across the spherical surface of the silver particle,  $k$  is the heat conductivity of water, and  $R$  is the radius of the particle. Based on this equation, the time constant should be over 30 ps.  $\tau_2$  and  $\tau_3$  are much faster than this, and the dependency on the polarization plane of pump and probe beams cannot be explained by a simple heat conduction. Thus we assigned  $\tau_2$  and  $\tau_3$  to ultrafast energy transfer before the energy transforms into heat. In Eqs. (1)–(5), we should read the temperature of silver particles ( $T_{\text{Ag}}$ ) for that of the photoexcited electrons ( $T_{\text{ele}}$ ) and the thermal conductivity ( $h_1$ ) for novel energy transfer coefficient. The polarization plane dependence of the second component ( $\tau_2$ : 3 ps) suggests that it accompanies an

orientational relaxation of water molecules at the surface of the particles. In the orientational relaxation process, the relaxation occurs by way of the orientation of water molecules, and the energy of the excited electrons is transferred to the water molecules, which are located at the interface. We consider the orientation of water molecules at the surface occurs to negate the induced dipole moment of silver particles after excitation. The third component ( $\tau_3$ : 7 ps) is considered to correspond to ultrafast energy transfer by photoexcited electrons. In this transfer process, the electrons which are not in equilibrium with the phonons interact with the interfacial solvent molecules, and through this interaction the energy is transferred. The change in the ULE signal in this case is due to the change in population of photoexcited electrons, i.e., the difference in refractive index between the excited state and the ground state contributes the ULE signal [17]. It is interesting to note that the photoexcited electrons remain out of equilibrium for up to 7 ps, because the electrons are expected to fully relax within 1 ps. Although further investigation is needed, this long life time of photoexcited electrons may have something to do with the anomalous phenomena of silver particles such as SERS. In our previous studies, some experimental results using transient reflectivity and transient reflecting grating indicated an ultrafast energy relaxation process involving hot electrons at solid/liquid interfaces [7,18]. These studies also support our present model.

Next, we discuss the time constants of the colloidal silver particles with SDS. The second component is assigned to ultrafast energy transfer by photoexcited electrons. The disappearance of the polarization-plane dependency is probably due to the adsorption layer of SDS molecules. The orientation of the water molecules by the induced dipole moment cannot occur because of the layer. The third component ( $\tau_3$ : 23 ps) is consistent with the rate assuming the conventional heat conduction from silver particles to solvent ( $\sim 30$  ps). Thus, we concluded that the third component corresponds to heat conduction from silver particles to the solvent by way of the adsorption layer of SDS molecules. Such heat transfer was not observed for the colloidal silver particles without SDS. This is probably because the adsorption layer of SDS molecules traps the hot

electrons and heat is generated at the adsorption layer. The direct energy transfer from the hot electrons to the solvent is thus disturbed by the adsorption layer.

In conclusion, ultrafast relaxation dynamics of silver ultrafine particles in aqueous solutions was measured using an ultrafast lensing effect (ULE) method. The relaxation dynamics was analyzed based on an energy transfer model from the particles to the solvent matrix. Our results indicate that ultrafast energy transfer processes (2–7 ps) faster than the conventional heat conduction ( $\sim 30$  ps) exist between the ultrafine silver particles and solvent molecules. This ultrafast energy transfer is assumed to be due to hot electrons, which are not in equilibrium with the lattice. We believe that the ULE technique will be a powerful tool to investigate the behavior of hot electrons in solutions.

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