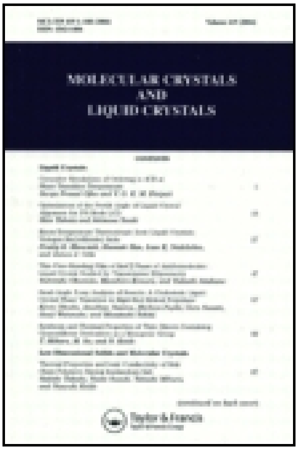

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Femtosecond Electronic Relaxation Dynamics in Metal Nano-Particles: Effects of Surface and Size Confinement

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FEMTOSECOND ELECTRONIC RELAXATION DYNAMICS IN METAL NANO-PARTICLES: EFFECTS OF SURFACE AND SIZE CONFINEMENT

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Abstract Direct measurements of the electron dynamics in gold colloidal nano-particles are performed using femtosecond laser spectroscopy. The small size of the particles is found to render electronic relaxation substantially slower (7 ps) than in gold thin films (1 ps). This is attributed to weaker electron-phonon coupling and less hot electron transport in small particles. This observation is qualitatively consistent with theory but, quantitatively, much less drastic than predicted. The discrepancy between experiment and theory is primarily attributed to surface imperfection.

INTRODUCTION

Metal nano-particles are interesting because of their novel electronic and optical properties, partly due to size confinement of the electronic wave function [1,2,3]. Since their size is usually smaller than the optical penetration depth and all the atoms in the particle are essentially "surface" atoms [4], they provide an intriguing system for probing the electron dynamics at liquid-metal interfaces [5]. Also, because their size is typically much smaller than the wavelength of light, transmission optical techniques can be used conveniently for their study. This paper reports new findings on gold colloidal nano-particles that show a size confinement effect on the electronic energy relaxation process. The small size is found to make the electronic relaxation much slower in gold colloidal particles than in thin films. This observation is in qualitative, but not quantitative, agreement with theoretical predictions. The discrepancy between our experiment and the theoretical predictions is attributed to the presence of adsorbates as well as defects on the particle surface and to some limitations of the theoretical models.

EXPERIMENTAL

The gold colloids were prepared by the method of Frens [6]. A 0.01% aqueous solution of $HAuCl_4$ (25 ml) was brought to 100°C and 0.75 ml of a 1% aqueous sodium citrate solution was then added. The solution turned from pale yellow to pale gray-blue to red in about 1 minute and was stirred at 100°C for an additional 5 minutes. Resulting gold colloids had an average diameter of 14 nm with a size distribution of about 10% standard deviation. The electronic absorption spectrum (shown in Fig. 1) is in excellent agreement with literature data. The absorption at 390 nm is primarily due to a transition from near the top of the d-band to the Fermi level [7]. The particle size was determined using transmission electron microscopy. The particle size can be varied by controlling the ratio of $HAuCl_4$ to sodium citrate [6].

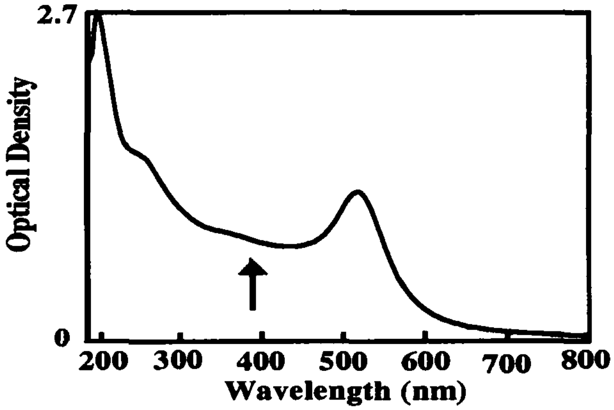

FIGURE 1. Electronic absorption spectra of a representative gold colloid. The arrow in the figure indicates the excitation wavelength (390 nm) used in the transient absorption experiment.

The dynamics measurements were performed using a pump-probe scheme with a regeneratively amplified, mode-locked femtosecond Ti-Sapphire laser system. The laser and the experimental setup have been described previously [8]. Pulses of 150 fs with a pulse energy of 250 μJ and center frequency at 780 nm were generated from a regeneratively amplified Ti-Sapphire laser system at 1 kHz. The output was doubled in a KDP crystal to generate 30 μJ/pulse of 390 nm light, which was used as a pump source to excite the colloids. The remaining fundamental was focused into quartz to generate a white light continuum and the desired probe wavelength was selected. The pump power was attenuated to such a level (about 20 μJ/pulse) that there was no signal from the pure solvent, i.e. water.

RESULTS AND DISCUSSION

Fig. 2 shows several transient absorption spectra of a representative gold colloid (14 nm particles), probed at 660 nm following excitation at 390 nm, on two different time scales and at three different excitation intensities. At high excitation intensities (Fig. 2a and b), the transient spectra feature a very fast rise followed by a double exponential decay with a fast and slow component. At low excitation intensity (Fig. 2c), the spectrum features a fast rise followed by a single exponential decay. All the data fit well to a single exponential rise with a time constant of 100 fs and a fast 7.0 (±0.5) ps exponential decay followed by a slower 400 (±50) ps exponential decay, convoluted with a 200 fs Gaussian representing the instrument response; only the amplitudes of the two decay components are different for the different excitation intensities (the amplitude for the slow component is zero for the low intensity data). It was found that the amplitude of the fast decay increases almost linearly with the excitation intensity while the amplitude for the slow 400 ps decay increases with the excitation intensity to the power of about 1.7. This indicates that the two decays are from electrons generated through two different mechanisms. We attribute the slow component to electrons ejected from the gold particles into the liquid through a two-photon ionization process, as explained in more detail elsewhere [9]. This paper deals primarily with the fast decay component, which is attributed mainly to electronic relaxation due to electron-phonon coupling.

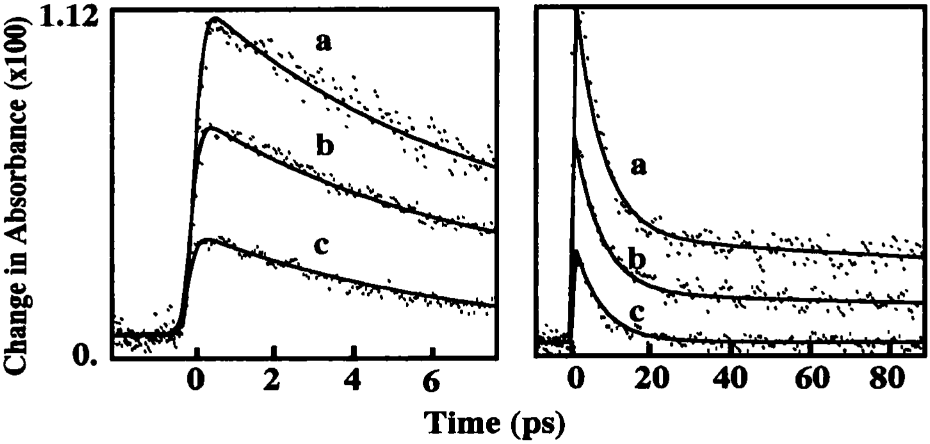

FIGURE 2. The time evolution of the photoinduced electrons probed at 660 nm following excitation at 390 nm on two different time scales and at different excitation intensities: a) 20 μJ/pulse, b) 14 μJ/pulse, and c) 7 μJ/pulse. The dotted lines are the experimental data. The solid lines are fits using a function discussed in the text.

In order to better understand the electronic relaxation mechanism and to explain the data obtained in gold colloidal nano-particles, we first compare our results to those observed in gold thin films. A series of experiments have been performed by Ippen, Fijimoto and co-workers [11-13] and by Elsayed-Ali *et al.* [10,14] to study the electronic relaxation dynamics in gold thin films using femtosecond reflection and thermomodulation techniques. It was found that the electronic relaxation due to electron-phonon coupling in gold films takes place with a time constant of 1-3 ps. A more recent study by Wang *et al.* [15] using femtosecond thermionic emission also found a relaxation time of 1.5 ps. These results are generally in good agreement with a theoretical model developed by Allen [16].

One important observation made by Brorson *et al.* [13] was that the decay was slower in a thinner gold film, which was attributed to less non-equilibrium electron transport in thinner films than in thicker films [13]. Their results were interpreted in the framework of a theoretical model developed by Kaganov *et al.* to explain electronic relaxation in metals [17]. It has been found that, when the film is thick (e.g. 100 nm) compared to the optical skin depth of around 15 nm, both hot electron diffusion and electron-phonon coupling are important in the electronic relaxation process and the decay is generally fast, 1 ps or less [13]. When the sample thickness (20 nm, the thinnest studied) is on the order of the optical skin depth, the decay is slower, about 2 ps, due to reduced hot electron transport [13]. The same argument can be used to explain our observation of a much slower decay, 7 ps, in gold nano-particles. Since in particles the spatial confinement is three dimensional, rather than one dimensional in thin films, less hot electron transport is expected, resulting in slower electronic relaxation than in the thin film with a thickness comparable to the diameter of the colloidal particles. ***Therefore, one possible explanation for the slower decay observed in nano-particles than in thin films is that there is less non-equilibrium electron transport due to the spatial size confinement of the electrons in three dimensions.***

We will next compare our results to some theoretical predictions of electronic relaxation in metal particles. Belotskii and Tomchuk have carried out a quantum-kinetic treatment of electron-phonon energy exchange in small metallic particles [18]. They predicted that the energy exchange between electrons and lattice phonons in small metallic particles is much weaker than in bulk metals, which is attributed to the fact that the electron oscillation frequency exceeds the Debye frequency of the phonon subsystem, thereby suppressing the electron-phonon interaction [19,20]. Using gold particles with a diameter of 20 nm as an example, they calculated that the electron-phonon coupling constant is about $2\text{x}10^{14}$ $\text{Wm}^{-3}\text{K}^{-1}$, which is two orders of magnitude smaller than the bulk value of $2\text{-}3.5\text{x}10^{16}$ $\text{Wm}^{-3}\text{K}^{-1}$ [11]. This theoretical result would suggest that the electronic relaxation time should be 100 times slower, or on the order of 200 ps, in gold metal particles than in the bulk (or thick films), since the electronic relaxation time is inversely proportional to the electron-phonon coupling constant [12,18]. Our observed 7 ps relaxation time in gold nano-particles with a similar size to that used in the calculation is thus significantly faster (about 30 times using the theoretical coupling constant [18]) than that predicted by this theoretical model. The discrepancy is most likely caused by the presence of surface adsorbates and defects, which were not accounted for in the theoretical model. The effect of the surface is further substantiated by the observation of a faster electronic relaxation time, 5 ps, in gold nano-particles dispersed in cyclohexane, which indicates a dependence of the relaxation time on the solvent or surface environment. It should also be noted that the theoretically calculated coupling constant is a factor of 2.5 smaller than that measured by the same authors [18,19], indicating that the theoretical model may have, to some extent, underestimated the electron-phonon coupling constant. *Therefore, another likely explanation for the observed slower decay in gold colloidal particles than in the bulk (or thick films) is weaker electron-phonon coupling.* By solving the two equations based on the diffusion model [17], we have found that electron-phonon coupling plays a more dominant role in electronic relaxation than hot electron diffusion.

The observation of a slower electronic relaxation process in gold colloid is similar to that in silver colloid. In aqueous silver colloid the electronic relaxation time, 2-3 ps [4], is a factor of 3 slower than in silver films, 670 fs [21]. It is interesting to note that in both silver and gold colloids the size confinement leads to slower electronic relaxation when compared to the respective thin films (essentially bulk in most studies conducted). This suggests the possibility that slower electronic relaxation in colloidal nano-particles, in comparison to their bulk, might be found in other metals as well.

We finally comment on the size dependence of the electronic relaxation dynamics. For gold colloids in the size range of 12-18 nm (diameter), we have found no noticeable size dependence of the decay dynamics, despite a strong size dependence suggested by theory: slower decay for smaller particles [18]. This is most likely because the increase in surface-to-volume ratio with decreasing size, coupled with adsorbates and defects on the particle surface, facilitates electronic relaxation. Preliminary data on particles with a significantly larger size (25 nm) actually show a considerably slower decay, 12 ps, than in the 14 nm particles. This seems to support the idea that the surface plays an important role in the electronic relaxation process.

CONCLUSIONS

In summary, the electronic energy relaxation in metal colloidal nano-paricles was found to be slower than in the bulk. This is attributed to a combination of weaker electron-phonon coupling and less hot electron transport in metal particles, both of which are direct consequences of the small size of the particles. The observation is consistent qualitatively, but not quantitatively, with theoretical predications. The discrepancy between experiment and theory was primarily attributed to the influence of surface imperfection due to adsorbates and defects.

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REFERENCES

1. V. Vijayakrishnan, A. Chainani, D. D. Sarma, and C. N. R. Rao, J. Phys. Chem., 96, 8679 (1992).
2. A. Henglein, J. Phys. Chem., 97, 5457 (1993).
3. W. P. Halperin, Rev. Mod. Phys., 58, 533 (1986).
4. T. W. Roberti, B. A. Smith, and J. Z. Zhang, J. Chem. Phys., 102, 3860 (1995).
5. G. L. Richmond, J. M. Robinson, and V. L. Shannon, Prog. Surf. Sci., 28, 1 (1988).
6. G. Frens, Nature: Physical Science, 241, 20 (1973).
7. N. E. Chsritensen and B. O. Seraphin, Solid State Commu., 8, 1221 (1970).
8. J. Z. Zhang, R. H. O'Neil, and T. W. Roberti, J. Phys. Chem., 98, 3859 (1994).
9. B. A. Smith, D. M. Waters, A. E. Faulhaber, M. A. Kreger, and J. Z. Zhang, J. Sol-Gel Sci. Tech., submitted, 1995.
10. H. E. Elsayed-Ali and T. Juhasz, Phys. Rev. B, 47, 13599 (1993).
11. R. W. Schoenlein, W. Z. Lin, J. G. Fujimoto, and G. L. Eesley, Phys. Rev. Lett., 58, 1680 (1987).
12. C.-K. Sun, F. Vallee, L. Acioli, E. P. Ippen and J. G. Fujimoto, Phys. Rev. B, 48, 12365 (1993).
13. S. D. Brorson, J. G. Fijimoto, and E. P. Ippen, Phys. Rev. Lett., 59, 1962 (1987).
14. H. E. Elsayed-Ali, T. Juhasz, G. O. Smith, and W. E. Bron, Phys. Rev. B, 43, 4488 (1991).
15. X. Y. Wang, D. M. Riffe, Y.-S. Lee, and M. C. Downer, Phys. Rev. B, 50, 8016 (1994).
16. P. B. Allen, Phys. Rev. Lett., 59, 1460 (1987).
17. M. I. Kaganov, I. M. Lifshitz and L. V. Tanatarov, Sov. Phys. JETP, 4, 173 (1957).
18. E. D. Belotskii and P. M. Tomchuk, Int. J. Electronics, 73, 955 (1992).
19. S. A. Gorban, S. A. Nepijko, and P. M. Tomchuk, Int. J. Electronics, 70, 485 (1991).
20. E. D. Belotskii and P. M. Tomchuk, Surface Science, 239, 143 (1990).
21. R. H. M. Groeneveld, R. Sprik, and A. Lagendijk, Phys. Rev. Lett., 64, 784 (1990).