Ultrafast time-resolved photoluminescence from novel metal–dendrimer nanocomposites

O. Varnavski and R. G. Ispasoiu
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

L. Balogh and D. Tomalia
Center for Biological Nanotechnology, University of Michigan Medical School, Ann Arbor, Michigan 48109

T. Goodson III[a)]
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

We report the first results of ultra-fast enhanced light emission from gold– and silver–dendrimer nanocomposites. There is a fast (70 fs) fluorescence decay component associated with the metal nanocomposites. Anisotropy measurements show that this fast component is depolarized. The enhanced emission is suggestively due to local field enhancement in the elongated metal–dendrimer nanoparticles. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1344231]

It is now well-accepted that future electronic and magnetic applications may involve the use of superior nanostructured materials such as transition metal nanoparticles.[1,2] It has been well-demonstrated that the electronic and magnetic properties of nanoparticles are strongly dependent on their size and shape.[3] Thus, the control of the particle's morphology is of critical concern for future applications. Dendrimer nanocomposites are a relatively new class of materials that hold great promise in this regard.[4] Dendrimers encapsulating transition metals have recently been prepared in which the metal nanoclusters are isolated by the dendrimer host system.[5–7] Due to their recently discovered ability to isolate and stabilize metal nanoclusters, organic dendrimers offer an opportunity to investigate the ultrafast dynamics of fundamental optical interactions in embedded metal nanoclusters.

Although several selected systems have produced various dynamical models for ultrafast excitations in nanoparticles,[8,9] there is a widely accepted general model that accounts for the majority of the events in the excitation and decay processes. This involves the optical excitation of the electrons by interband and intraband transitions. These processes are then followed by a loss of coherence, which is largely due to electron–electron and electron–surface scattering processes that result in a quasi-equilibrated electron system that normally has a duration of approximately 100 fs. The hot electron system can also lose its energy through electron–phonon coupling.[10,11] There have been several reports of the time-resolved transient absorption effects in metal nanoparticles. Utilizing time-resolved transient absorption several reports have clarified a large degree of the complexity of ultrafast optical excitations in nanoparticles. These studies can only identify the recurrence of the ground state electronic structure. Certainly, there is more to be learned from the emission properties of nanoparticles.

The fluorescence from bulk metal (Au) with an extremely low efficiency of 10^{-10} was first observed by Mooradian.[12] While several groups have recently demonstrated that nanoparticles exhibit an increase (compared to bulk) of the fluorescence quantum efficiency,[8,13] the quantum efficiency of metal nanoparticles is still very low so that the actual fluorescence signal is difficult to measure. Presently, there have been no reports of time-resolved fluorescence from transition metals. The characteristic size and separation of core clusters in dendrimer nanoparticle systems may play a large role in the ability to observe the emission resulting from the optical excitation process. In this communication we report the first ultrafast time-resolved emission investigation in a dendrimer transition metal nanocomposite system. This is also the first report of the anisotropy decay in a metal nanocomposite system.

The structures under investigation were Au– and Ag–dendrimer nanocomposites, $\{Au(0)\}_I$, formally called ($\{(Au(0)_{10.01}\text{-PAMAM\_E5.NH}_2\})$ and $\{Ag(0)\}_I$, formally called $\{Ag(0)_{26.9}\text{-PAMAM\_E4.TRIS}\}$, respectively in which the dendrimer template molecule was polyaminoamine (PAMAM).[5,6] High resolution transmission electron microscopy (HRTEM) revealed that the guest-metal domains in this particular system can form clusters with sizes distributed around 15 nm.[5,6]

Femtosecond up-conversion spectroscopy was employed to temporally resolve the polarized fluorescence of the metal–dendrimer nanocomposites. Our optical arrangement for the up-conversion experiments has been described previously.[14,15] The full width at half maximum (FWHM) of the pulse cross-correlation function at 790 nm was estimated to be ~200 fs. The energy of the excitation pulse did not exceed 0.5 nJ/pulse. The measured fluorescence decay curves were fit to the result of the convolution of the instrument response function with an exponential decay model in order to minimize the sum of weighted residuals (χ^2).[16]

Shown in Fig. 1 is the time-resolved emission from (a) $\{Ag(0)\}_I$ and (b) $\{Au(0)\}_I$ for excitation at 395 nm. It can be seen that there are two components in the dynamics of the emission signal. One of these decay components is comparable in duration with the width of instrument response func-

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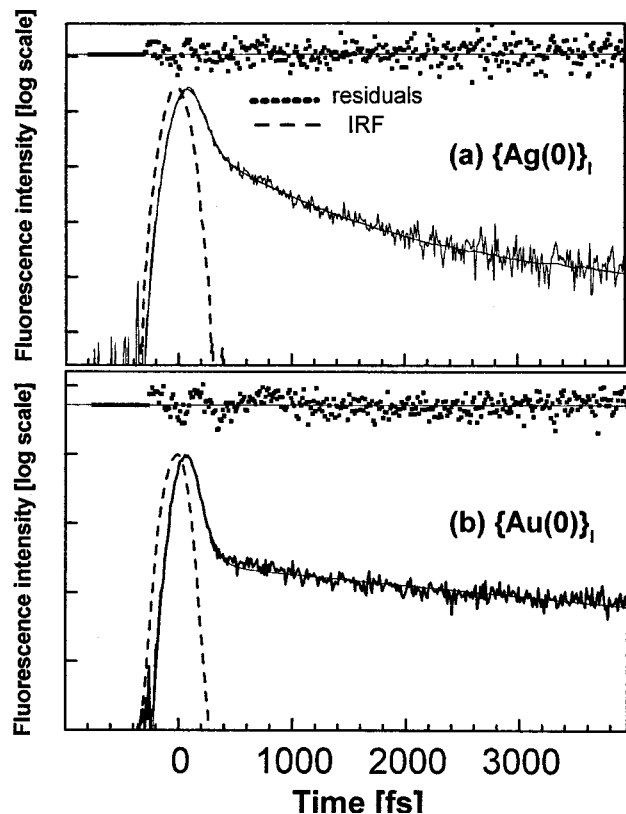[a)]Author to whom correspondence should be addressed. Electronic mail: tgoodson@chem.wayne.edu

FIG. 1. Fluorescence dynamics of (a) $\{Ag(0)\}_I$, and (b) $\{Au(0)\}_I$, for excitation at 395 nm, and emission at 480 and 570 nm, respectively. The corresponding numerical fits to the data are indicated by the thin solid lines.

FIG. 2. Schematic illustration of the dynamics of the photoluminescence from the $\{Au(0)\}_I$ system. The inset shows the comparison of the $\{Au(0)\}_I$ SP absorption peak with the spectral distribution of the $\{Au(0)\}_I$ emission peak for excitation at 3.14 eV (395 nm).

tion (IRF) (also shown in Fig. 1) while the second one is relatively long, on a time scale of several picoseconds. Indeed the decay curve for gold nanocomposites could be reasonably fit by a two-exponential decay function with time constants of 75 fs, and 5.5 ps with relative amplitudes of 0.95 and 0.05, respectively. The silver–dendrimer nanocomposite fluorescence decay exhibited an additional intermediate component (as was deduced from the fitting analysis) and had lifetimes of 70 fs, 700 fs, and 5.3 ps.

The time-resolved intensity of emission from the dendrimer nanocomposites was found to be relatively large. It was only two orders-of-magnitude smaller than that of the organic dye we commonly use as a standard with high quantum efficiency. Considering the short fluorescence lifetime of dendrimer nanocomposites, the fluorescence efficiency can be estimated to be larger than 10^{-7}. This is three orders-of-magnitude higher than that for a bulk metal.[12] The fact that the time-resolved emission from the transition metal nanoparticle was not be observed previously may be related to interactions of the dendrimer isolating host with metal nanoclusters. Dendrimers may cause changes in the shape and size of the metal nanoparticles as well as the interface boundary conditions.[17] The sizes of the metal domains as estimated by HRTEM are distributed around ~15 nm, whereas the diameter of the PAMAM dendrimer (5th generation) is ~6 nm.[6,7] It is well-known that for small particles (less than 3 nm) surface plasmon absorption peak is very small.[7,17] However, in our system the surface plasmon peak is intense and clearly seen (see inset to Fig. 2) suggesting a particle size
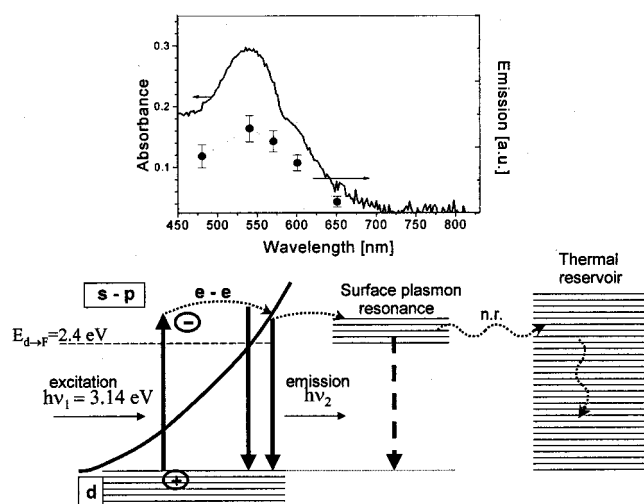
larger than 3 nm. This result indicates that the metal nanoclusters extend beyond the diameter of the dendrimer host which is in agreement with the HRTEM image.[5,6] It can be assumed that the formation of nanoparticles aggregates or structures resembling percolation clusters is possible.

Recently Mohamed and co-workers reported a drastic increase (a million times) of the fluorescence from elongated gold nanoparticles as compared to spherical particles.[8] This elongation associated with the formation of nonspherical clusters may also be the case for the present dendrimer nanocomposite system's detectable time-resolved emission. The surface plasmon (SP) resonance peak in the absorption spectrum of the Au–dendrimer nanocomposite is shown (solid line) in the inset of Fig. 2, together with the spectral distribution of the peak amplitude of the time-resolved luminescence signal (dotted line and diamonds) from the $\{Au(0)\}_I$ nanocomposite. A weak shoulder on the long wavelength side of SP resonance is clearly seen in Fig. 2. Comparing this shoulder with the calculations and experimental result reported by Mohamed et al.[8] we can conclude that the mean aspect ratio for our nonspherical particles is relatively small and/or distribution of particle lengths is rather broad. Indeed, the HRTEM showed the variety of particle shapes while the particle size distribution at half maximum extended from 5 to 25 nm.[5,6] It was reported[8] that even for slightly elongated particles with the aspect ratios about two, emission enhancement relative to the bulk metal still may exceed a factor of 10 000. The fluorescence maximum in this case can be very close to the transverse surface plasmon resonance. In our case we estimated the enhancement factor to be about 1000. At the same time, the maximum of emission intensity was found to be close to SP resonance (Fig. 2).

Previous reports of CW fluorescence from bulk metals[12] as well as from metal nanoparticles embedded in micelles[8] have assigned the fluorescence as originating from the recombination of electrons in the $s-p$ band with holes in the d
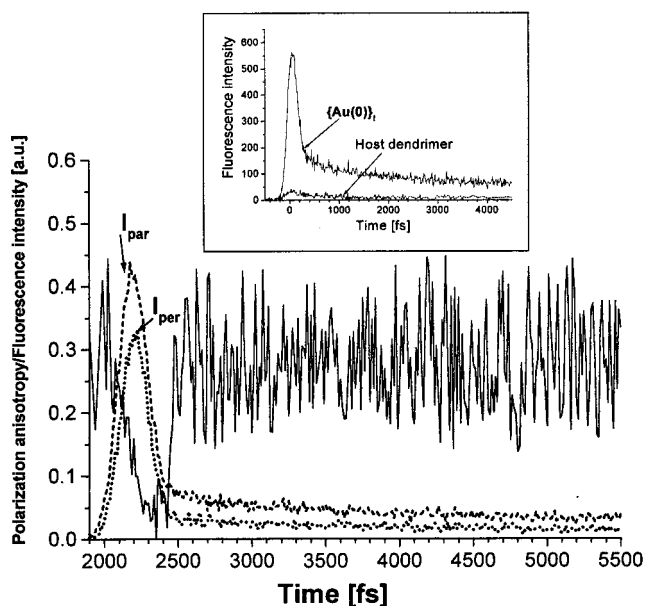
FIG. 3. The dynamics of the polarization anisotropy for the $\{Au(0)\}_I$ emission. The inset shows the comparison of the $\{Au(0)\}_I$ fluorescence dynamics with that of the pure dendrimer host.

band. In Fig. 2 we show a schematic diagram summarizing the sequence of excitation and relaxation mechanisms involving transitions between the d and $s-p$ bands in Au nanoparticles. There are various channels for nonradiative decay following the quenching of fluorescence. These processes involve electron–phonon coupling as well as the coupling of the metal nanoparticles to the thermal reservoir of the dendrimer host.[18] An alternative mechanism for the observed ultrafast emission could be the interaction of the emission dipole moment of the metal SP resonance with the emission dipole moment of the dendrimer host (surface-enhanced fluorescence).[19]

The fluorescence polarization anisotropy is used to provide information about the dipolar orientational dynamics occurring after the excitation of the system. The detected emission intensities I_{par}, I_{per} for parallel and perpendicularly polarized excitation, respectively, were used to construct an observable emission anisotropy $R(t)$ in accordance with the equation

$$R(t) = \frac{I_{par}(t) - GI_{per}(t)}{I_{par}(t) + 2GI_{per}(t)}. \tag{1}$$

The factor G accounts for the difference in sensitivities for the detection of emission in the perpendicular and parallel polarized configurations. We evaluated this factor from our test measurements of fast rotational diffusion of perylene in solution.[16]

The anisotropy decay result for $\{Au(0)\}_I$ is shown in Fig. 3. The temporal profiles of the emission in the parallel plane (dashed line) and the plane perpendicular (dotted line) to the polarization of the excitation pulse are shown. It is clearly seen that polarization state of the emission during the first 300 fs after excitation is quite different from that for longer times. The ''dip'' and ''rise'' in the anisotropy curve usually suggest that there is more than one species in the system

whose contributions to the effective $R(t)$ have different time scales.[20] Indeed, depolarized emission was observed for metals[12] while initially highly polarized emission is typical for organics.[20] From these observations we can attribute the polarized long decay to the emission of the dendrimer template and the fast (and nearly depolarized) component to the emission of the metal nanoparticle. This result is in agreement with the measurements of the pure dendrimer's fluorescence decay. It is also interesting to note that the long (polarized) component of the dendrimer metal nanocomposite is much larger in amplitude than the decay of the pristine dendrimer host (see inset to Fig. 3). The shape of the two curves is the same, however the long component fluorescence of the metal dendrimer nanocomposite is stronger. This may imply that the metal particle enhances the emission of the host dendrimer molecules due to surface enhancement effect.[19]

The finite length of the instrument response function distorts I_{par} and I_{per} from their true decay profiles. Consequently this distorts the $R(t)$ as well, especially in the vicinity of the IRF.[20,21] Nevertheless, a reasonable estimate can be made by use of a simple model of single exponential decay for the isotropic emission (with a time constant τ_F) and for anisotropic emission (with a time constant τ_r). We convoluted the IRF with these model functions to obtain the ratio of the intensities I_{par}/I_{per}. The fluorescence decay time τ_F was obtained as a result of the fitting procedure of the isotropic decay described above. Calculations were made for an initial anisotropy of 0.4 which corresponds to the case of a highly asymmetrical nanoparticle with a transition dipole moment whose orientation is strongly associated with the nanoparticle geometry.[22,23] A comparison of the model calculations with the experimental ratio of intensities showed that the anisotropy decay time ($\sim$20 fs) should be 3 to 4 times shorter than the isotropic decay time ($\sim$75 fs). This difference between the isotropic and anisotropic decay times suggests that two mechanisms may be responsible for these decay processes (such as electron–electron and electron–surface scattering).

In conclusion we have measured the time-resolved fluorescence from metal dendritic nanocomposites. To our knowledge this is the first report of the fast fluorescence dynamics from metal nanoparticles. The dendrimer architecture allows for strongly enhanced measurable fluorescence intensity from the metal nanoclusters. We have demonstrated, by fluorescence anisotropy measurements, that the metal emission shows a depolarized character while the dendrimer host shows a relatively polarized emission. The isotropic fluorescence decay was found to be much slower than the depolarization rate. The proposed mechanism of the emission decay is due to electron–electron and electron–surface scattering processes, and there may also be a contribution from the interaction of emission dipoles of the dendrimer host and surface plasmon of the metal. We found that the emission decay was faster than what is expected for a phonon coupling process with a characteristic time constant of $\sim$1 ps.[9] Thus, electron–phonon scattering is not likely to contribute to the emission decay we observed for these novel metal dendrimer nanocomposites. These results bring about the opportunities for investigations of new physics concern-

ing the interactions of metal nanoparticles with macromolecules.

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