Published in final edited form as:

J Phys Chem C Nanomater Interfaces. 2008 October 22; 112(46): 17931–17939. doi:10.1021/jp8065647.

Luminescence Decay Dynamics and Trace Biomaterials Detection Potential of Surface-Functionalized Nanoparticles

Kwan H. Cheng^{†,*}, Jacob Aijmo[†], Lun Ma^{TEL}, Mingzhen Yao^{TEL}, Xing Zhang^{TEL}, John Como[†], Louisa J. Hope-Weeks[§], Juyang Huang[†], and Wei Chen^{TEL,†}

[†]Department of Physics, Texas Tech University, Lubbock, Texas 79409

^{TEL}Department of Physics, The University of Texas at Arlington, Arlington, Texas 79019

[§]Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Abstract

We have studied the luminescence decay and trace biomaterials detection potential of two surface-functionalized nanoparticles, poly(ethylene glycol) bis(carboxymethyl) ether-coated LaF₃:Ce,Tb (~20 nm) and thioglycolic acid-coated ZnS/Mn (~5 nm). Upon UV excitation, these nanoparticles emitted fluorescence peaking at 540 and 597 nm, respectively, in solution. Fluorescence imaging revealed that these nanoparticles targeted the trace biomaterials from fingerprints that were deposited on various nonporous solid substrates. Highly ordered, microscopic sweat pores within the friction ridges of the fingerprints were labeled with good spatial resolutions by the nanoparticles on aluminum and polymethylpentene substrates, but not on glass or quartz. In solution, these nanoparticles exhibited multicomponent fluorescence decays of resolved lifetimes ranging from nano-to microseconds and of average lifetimes of ~24 and 130 μs for the coated LaF₃:Ce,Tb and ZnS:Mn, respectively. The long microsecond-decay components are associated with the emitters at or near the nanocrystal core surface that are sensitive to the size, surface-functionalization, and solvent exposure of the nanoparticles. When the nanoparticles were bound to the surface of a solid substrate and in the dried state, a decrease in the microsecond decay lifetimes was observed, indicative of a change in the coating environment of the nanocrystal surface upon binding and solvent removal. The average decay lifetimes for the surface-bound ZnS:Mn in the dried state were ~60, 30, and 11 μs on quartz, aluminum, and polymethylpentene, respectively. These values were still 2 orders of magnitude longer than the typical fluorescence decay background of most substrates (e.g., ~0.36 μs for polymethylpentene) in trace forensic evidence detections. We conclude that coated ZnS: Mn nanoparticles hold great promise as a nontoxic labeling agent for ultrasensitive, time-gated, trace evidence detections in nanoforensic applications.

Introduction

Highly luminescent nanoparticles have been extensively studied in recent years due to their potential applications in advanced solid state lighting, biomaterials characterizations, detection and imaging, medical diagnostics, and targeted therapeutics.^{1–3} Most reaction processes of labeling compounds with target biomaterials require the presence of water.¹ In this respect, site-specific, photostable, and water-soluble nanoparticles are needed for achieving ultrasensitive labeling and detection of biomaterials. Most of the current applications of water-soluble nanoparticles have been focused on biomedical applications, particularly on cell and

tissue labeling and imaging.² The potential applications of site-specific, water-soluble nanoparticles for forensic applications, particularly trace evidence detection by ultrasensitive chemical labeling of biomaterials on the surface, have not been fully explored.

Water-soluble nanoparticles with protein labeling functionalities and long luminescence decay times are important for achieving ultrasensitive chemical labeling of trace biomaterials; for example, fingerprint-derived biomaterials deposited on substrates, in our case, on substrates with high fluorescence background.^{4,5} By capping the water-insoluble nanocrystalline core with various stabilizing agents, different chemical functionalities can be introduced to the surface of the nanoparticles to achieve chemical labeling of the biomaterials, for example, protein residues deposited by the fingerprints on a solid substrate. The long decay lifetime of the nanoparticles is an important feature necessary for ultrasensitive detections. Due to the strong luminescence background of the surface and the trace amount⁶ of target biomaterials to be detected on the surface, an efficient background suppression strategy is needed. In this respect, a time-gated luminescence detection method has been proposed.⁴ Using a pulsed excitation, the fluorescence image of the long-lived fluorescence emission from the labeled materials can be collected at a time window such that the short-lived fluorescence emission from the background has significantly decayed. Therefore, the decay lifetime of nanoparticles has to be much greater than that of the background. The latter is usually in the range of nanoseconds.⁴

Capped or surface-functionalized cadmium-based nanoparticles^{7–9} have been investigated for their potential to label and detect trace biomaterials on latent fingerprints. However, the decay lifetime of cadmium-based nanoparticles is usually less than 1 μ s. Recently, various surface-functionalized nanophosphors (e.g., doped LaF_3 and ZnS) have been developed for therapeutic and optical device applications.^{10–20} These doped nanoparticles exhibit fluorescence decay lifetimes in the microseconds or longer region. In addition, some of these nanoparticles (e.g., doped ZnS) are nontoxic and environmentally friendly.²¹ These long decay lifetime and nontoxic nanoparticles therefore hold great promise as labeling agents for the future development of ultrasensitive chemical detection and imaging of trace biomaterials on various substrates.

In this study, we examined two different surface functionalized nanoparticles, poly(ethylene glycol) bis(carboxymethyl) ether (COOH-PEG-COOH)-coated $\text{LaF}_3\text{:Ce,Tb}$ and thioglycolic acid (TGA)-coated ZnS:Mn . They are all water-soluble and have the common surface-reactive carboxylic (–COOH) functional group capable of labeling the amide group of the target biomaterials, mainly proteins. Depending on the synthesis conditions and surface-functionalization, the fluorescence emission of these nanoparticles exhibited very complex or multi-component decay behavior, and the intensity-averaged decay lifetime of these nanoparticles was around microseconds or longer.^{3,5,18,22–27}

In this work, the labeling specificity of these nanoparticles on trace biomaterials was demonstrated by comparing the protein labeling patterns of the fingerprints on several solid substrates: aluminum, glass, quartz, and polymethylpentene plastic. To evaluate the potential of these nanoparticles as labeling agents for ultrasensitive and time-gate imaging of nanoparticles for trace biomaterials detections, we have also carefully characterized the luminescence decay dynamics of nanoparticles both in solution and also in the surface-bound, air-dried state. Although a significant decrease in the fluorescence lifetime of the nanoparticles occurred when they were bound to the surface, the averaged decay lifetimes of TGA-coated ZnS:Mn nanoparticles were within 10–60 μ s. These decay lifetimes values were still several orders of magnitude longer than the decay lifetime from a highly fluorescence polymethylpentene substrate (control) in our work. This study demonstrated the significant potential of surface-functionalized ZnS:Mn nanoparticles as a nontoxic fluorescence labeling

agent for future ultrasensitive, background-suppressed, time-gated detection of trace biomaterials⁴ deposited on surfaces.

Materials and Methods

Synthesis of Surface-Functionalized Nanoparticles

COOH-PEG-COOH-LaF₃:Ce,Tb—Lanthanum nitrate (La₃(NO₃)₃·6H₂O, 99.99%), cerium nitrate (Ce(NO₃)₃·6H₂O, 99.99%), terbium chloride (TbCl₃·6H₂O, 99.99%), ammonium fluoride (NH₄F, 98%), and poly(ethylene glycol) bis(carboxymethyl) ether (COOH-PEG-COOH, 99%) were obtained from Sigma-Aldrich (St. Louis, MO) and used as received. Water-soluble Ce³⁺- and Tb³⁺-doped LaF₃ nanoparticles (La_{0.4}Ce_{0.45}Tb_{0.15}F₃) stabilized with COOH-PEG-COOH were synthesized as previously reported.¹⁹ Briefly, 1.6 mmol of La(NO₃)₃·6H₂O, 1.8 mmol of Ce(NO₃)₃·6H₂O, 0.6 mmol of TbCl₃·6H₂O, and 3.3 mmol of COOH-PEG-COOH were dissolved in 90 mL of distilled water, then 10 mL of NH₄F (10.5 mmol) was added dropwise under stirring at room temperature. After another 2 h of stirring, the solution was centrifuged, washed with deionized water three times, and dried at room temperature. The solid product obtained was then redissolved in deionized water, and a water-soluble nanoparticle solution was then formed. The pH value of the nanoparticle solution was around 7.50. The quantum yield of the nanoparticles was about 0.25.

TGA-ZnS:Mn—Zinc acetate (Zn(CH₃COO)₂·2H₂O, 99.99%), manganese acetylacetonate ((C₅H₈O₂)₂Mn, 99.9%), thioacetamide (CH₃CSNH₂, 99%), sodium hydroxide (NaOH, 98%), and TGA (HSCH₂COOH, 98%) were also obtained from Sigma (St. Louis, MO), and used as received. Water-soluble Mn-doped ZnS nanoparticles (ZnS:Mn) stabilized with TGA were prepared using the following steps: First, 0.5 g of Zn(CH₃COO)₂·2H₂O and 0.025 g of CH₃COO)₂Mn·4H₂O were dissolved in 125 mL of water. Second, 0.396 mL of TGA was added to the above solution, and the pH was adjusted to ~9 using a 0.1 M NaOH solution. The solution was then purged with nitrogen for at least 30 min. Third, 0.4 g of CH₃CSNH₂ was added to the solution with constant stirring to form a white solution in which ZnS nanocrystal nuclei were evident upon completion of the reaction. Last, the solution was refluxed at 100 °C for about 6 h to promote crystal growth, and the TGA-ZnS:Mn nanoparticles were obtained. The pH value of the nanoparticle solution was around 7.50. The quantum yield of the nanoparticles was about 0.20.

High Resolution Transmission Electron Microscopy Characterizations

High resolution transmission electron microscopy (HRTEM) images were obtained from a JEM-2100 TEM (JEOL, Tokyo, Japan) with an accelerating voltage of 200 kV. Samples for HRTEM measurements were prepared by depositing a drop of the nanoparticle solution onto a carbon-coated copper grid, and the excess liquid was wiped off with a filter paper. After drying the grid in air, HRTEM images were collected.

UV-Visible and Fluorescence Spectra

The UV-visible absorption spectra were recorded using a Shimadzu UV-2450 UV-vis spectrophotometer or a HP8453 (Agilent Technologies, Inc., Santa Clara, CA) spectrophotometer. The fluorescence emission and excitation spectra were measured using a Shimadzu RF-5301PC fluorometer or a QuantaMaster C61/2000 (PTI, Inc., Lawrenceville, NJ) spectrofluorometer.

Frequency-Domain Fluorescence Decay Measurements

Fluorescence decay lifetime measurements were performed on an ISS GREG 200 (ISS, Champaign, IL) fluorometer equipped with digital multifrequency cross-correlation phase and

modulation acquisition electronics.²⁸ A Liconix 4240NB cw UV He–Cd laser (Santa Clara, CA) operating at 325 nm was used as an excitation source. The intensity of the laser beam was modulated with a pockels cell. Fluorescence emission was collected through a 350-nm, low-cutoff filter using an L-format arrangement. An excitation polarizer with its transmission axis set at 35° with respect to the vertical was placed in the excitation beam to eliminate the contribution of the rotational diffusion effect of the sample to the measurements.²⁹ No polarizer was placed on the emission side. Frequency-domain data (i.e., demodulation (M) and phase difference (θ) values of the fluorescence emission signal from the sample, as compared with that of a standard solution of *p*-bis[2-(5-phenyloxzaolyl)]benzene (POPOP) in ethanol (decay lifetime = 1.34 ns) were collected as a function of intensity modulation frequency (f) of the excitation laser. The theory behind the frequency-domain fluorescence decay measurement has been described elsewhere.³⁰ Briefly, a delta-response fluorescence intensity decay $I(t)$ of a fluorescence sample is related to the harmonic-response fluorescence intensity function $\Phi(f)$ of the same sample by a Laplace transformation. Here, the measured demodulation $M(f)$ and phase shift $\theta(f)$ data are simply the amplitude and phase angle of the above $\Phi(f)$, respectively. The time-domain fluorescence decay information (e.g., the decay parameters of a multiexponential decay function (see below)) can be obtained by fitting the frequency-domain data with a decay function using nonlinear regression.³⁰ Our frequency-domain instrument operated on a modulation frequency range from 0.1 to 100 MHz and with nominal uncertainties of ± 0.01 and 0.02 for the demodulation and phase difference detections, respectively. Accordingly, the longest and shortest decay lifetimes our instrument could measure were ~ 50 ps and 200 μ s, respectively.^{28,30}

We modeled the intensity decay $I(t)$ of our nanoparticles in solution and the air-dried state with a multiexponential decay function as shown in eq 1, where n is the total number of decay components, and α_i and τ_i denote the molar fraction and the decay lifetime, respectively, of the i th decaying species of the sample. The intensity fraction f_i of the i th component and the intensity-weighted averaged fluorescence lifetime ($\langle \tau \rangle$) can be determined from eq 2 and eq 3, respectively.

$$I(t) = \sum_{i=1}^n \alpha_i e^{-t/\tau_i} \quad (1)$$

$$f_i = \frac{\alpha_i \tau_i}{\sum_{i=1}^n \alpha_i \tau_i} \quad (2)$$

$$\langle \tau \rangle = \sum_{i=1}^n f_i \tau_i \quad (3)$$

Deposition and Fluorescence Detection of Trace Biomaterials on Solid Substrates

Latent fingerprint residues were employed as a testing platform to assess the fluorescence labeling efficiency of our nanoparticles to trace biomaterials deposited on nonporous solid substrates. Detailed descriptions of applying latent fingerprints on different substrates have been reported previously.^{6,31,32} Briefly, latent fingerprints were prepared by pressing the fingers gently on different substrates, a 2.56 cm $\times$ 2.56 cm thin aluminum foil (Reynolds Metals Co., Richmond, VA), a precleaned plain 2.56 cm $\times$ 7.68 cm micro glass slide (Catalogue no.

34600, Kimble Glass Inc., Vineland, NJ), and a 100-mm diameter polymethylpentene plastic Petri Dish (Catalogue no. 5500-0010, Nalgene Labware, Rochester, NY). A drop (~1 mL) of nanoparticle solution was then added to the surface with the deposited fingermark. After a reaction time ranging from 20 min to 2 h, the nanoparticles were removed and the labeling surface was gently rinsed with DI water. The surface was allowed to air-dry for 20–30 min before imaging. A hand-held 6 W UV lamp (UVGL-58, UVP, Inc., Upland, CA) with emission at 254 nm was used for the fluorescence excitation of the labeled fingerprints. A Canon PowerShot S3 IS digital camera (Canon Inc., Lake Success, NY) coupled to an Olympus SZ-STS stereoscope (Tokyo, Japan) was used for imaging. Digital images in 24-bit color JPEG format were further analyzed by ImageJ³³ for brightness and contrast adjustment and scale bar determination.

Results

Chemical Compositions and Structures of Nanoparticles

Two different types of water-soluble, surface-functionalized nanoparticles (X-NP) were synthesized and studied. Here, X is the surface chemical group, COOH-PEG-COOH or TGA, that forms the water-soluble and stabilization layer surrounding the water-insoluble nanoparticle core (NP), LaF₃:Ce,Tb or ZnS:Mn, as shown in Figure 1. Although the two X-NP's have very different chemical compositions at their nanocrystalline cores and on the surface levels, they all have the same water-soluble and highly surface-reactive carboxylic (–COOH) functional subgroup(s) in X. This surface carboxylic group of X-NP can readily react with a primary amine group (–NH₂) of the target biomaterials via the amidation reaction.^{8,9} Other chemical reactions and interactions are also possible. Therefore, the surface chemical group X renders the water-soluble stabilization of the nanocrystalline core and, importantly, the chemical-labeling characteristics of the X-NP.

HRTEM Studies

A representative HRTEM image of the coated LaF₃:Ce,Tb nanoparticles is shown in Figure 2A. Here, most of the particles are spherical with a diameter around 20 nm, and a few are rod-shaped. The particles are highly crystalline, as evidenced by the clear lattice fringes from the [121] and [211] planes. From these fringes, the atomic plane distance was measured and found to be around 0.33 nm. This value is very close to the plane distance of 0.32 nm recently reported by Yanes et al.³⁴ using X-ray diffraction (XRD). A representative HRTEM image of the ZnS:Mn nanoparticles is also displayed in Figure 2B. The average size of the particles was about 5 nm, in good agreement with the XRD measurements on uncoated ZnS:Mn reported earlier.^{35,36} The lattice fringes from the [111] planes of some particles were clearly found in the HRTEM image with a measured atomic plane distance³⁶ of 0.31 nm. Again, this value is consistent with the [111] spacing of ZnS:Mn published previously.³⁶

Steady-State Spectroscopic Characterizations

Spectral characterizations of coated LaF₃:Ce,Tb nanoparticles in solution were performed at room temperature, as shown in Figure 3A. To better quantitate the wavelength location of the exciton absorption peak, a first-order derivative absorbance spectrum was calculated. Here, a peak and a dip, signifying the rise and fall, respectively, of the slope of the absorbance with increasing wavelength, were evident in the derivative spectrum (Figure 3A insert). The wavelength locations of the peak and dip were further determined by the local maximum and minimum of the 2-pass–5-point running averages of the derivative values, respectively. Note that this multiple-pass data smoothing protocol³⁷ effectively suppressed data scatter due to random errors of UV–visible measurements. The midpoint between the resolved peak and the dip from the derivative spectrum was subsequently determined (i.e., 307 nm in this case) to define the precise wavelength location (marked by an arrow) of the poorly resolved exciton

peak in the original absorbance spectrum. The fluorescence excitation spectrum exhibited a prominent peak at 276 nm and several small but significant peaks at 344, 354, 372, and 380 nm. The fluorescence emission spectrum revealed four well-resolved peaks at 487, 540, 584, and 622 nm, with 540 nm being the major one, and two very small but significant peaks at 334 and 363 nm. The above spectral peak locations are summarized in Table 1. In addition, the spectral assignments of these peaks were identified by comparing our results with the known emission and excitation spectra of Ce^{3+} in a SrF_2 crystal and of Tb^{3+} in $\text{Gd}_2\text{TeO}_6:\text{Tb}^{3+}$ phosphor.^{38,39}

The spectral features of coated $\text{ZnS}:\text{Mn}$ nanoparticles are shown in Figure 3B. Here, the exciton peak was found at 283 nm using the same peak identification procedure as above. For the fluorescence excitation spectrum, a small shoulder at around 275 nm and a prominent peak at 324 nm were evident. For the emission spectrum, two broad peaks centered at 441 and 597 nm were observed. The fluorescence excitation and emission spectra of a polymethylpentene plastic sheet were also collected, as shown in Figure 3C. Here, an excitation peak at 320 nm and an emission peak at 372 nm but with a long wavelength tail were observed. The locations and spectral assignments of the peaks are displayed in Table 1.

Labeling of Trace Biomaterials on Surfaces by Nanoparticles

Figure 4 shows the representative nanoparticle labeled fingerprint images on different substrates. Fingerprint residues were deposited on three different solid substrates (aluminum, glass, and polymethylpentene plastic), and solutions of the coated nanoparticles were used to label the trace biomaterials derived from the fingerprints (see Materials and Methods). Fingerprints on aluminum, glass, and plastic labeled by the coated $\text{LaF}_3:\text{Ce},\text{Tb}$ nanoparticles are shown in Figure 4A, B, and C, respectively. Bright dots representing the sweat pores within the friction ridges of the fingermarks were clearly evident on the aluminum and plastic surfaces. However, only the labeled friction ridges were observed on the glass surface. Similar observations of the specific sweat pore labeling were found for the fingerprints labeled by the coated $\text{ZnS}:\text{Mn}$ nanoparticles, as shown in Figure 4D, E, and F. A labeling time of ~ 2 h was needed for developing the fingerprints on all substrates for both types of nanoparticles, except the fingerprints on aluminum using the coated $\text{ZnS}:\text{Mn}$ nanoparticles that required a short 20-min labeling time. Longer labeling time for the latter produced extensive nonspecific binding of the nanoparticles to the metal and resulted in poor labeling of the fingerprint residues. Quartz was also used as a substrate, and labeling results were similar (results not shown) to those on glass for both nanoparticles.

Time-Resolved Fluorescence Decay Characterizations

Time-resolved fluorescence decay measurements of surface-functionalized nanoparticles in solution and at room temperature were performed using the frequency domain method. The fluorescence decay profile of the coated $\text{LaF}_3:\text{Ce},\text{Tb}$ nanoparticles in solution was first examined as shown in Figure 5. Multiexponential decay fits to the frequency domain data were performed, and the recovered intensity decay parameters (τ 's and β 's) are summarized in Table 2. The data-fitting improved with an increasing number of decay components from 1 to 4, as demonstrated in Figure 5, and the fast convergence of the χ^2 value as given in Table 2. Note that the use of more than five decay components or more than nine fitting parameters did not improve the quality of the fit significantly, as judged by the χ^2 values (results not shown). In some cases, overfits (i.e., multiple decay lifetimes of similar values but with different intensity fractions) were observed. A similar multicomponent decay analysis was also performed on the frequency domain data of $\text{ZnS}:\text{Mn}$ in solution, and four distinct lifetime decay components were also resolved, as shown in Table 3.

The longest resolved fluorescence decay lifetime (τ_1) for our nanoparticles was in the microsecond range (i.e., ~70 and 130 μ s for LaF₃:Ce,Tb and ZnS:Mn, respectively), as shown in Table 2 and Table 3. The other resolved lifetimes can further be classified into three distinctive ranges: 30–150, 4–15, and 0–1 ns. The longest decay lifetime of the coated LaF₃:Ce,Tb made up ~40% of the total intensity, whereas that of the ZnS:Mn constituted more than 90% of the total intensity. Since two well-separated fluorescence emission peaks were observed in the coated ZnS:Mn, fluorescence decays from the 441 and 597 nm peaks were separately measured using a 400–500 nm band-pass and a 530 nm long-pass filter, respectively. Only three lifetime decays were sufficient to fit the decay data in both cases. As shown in Table 3, the fluorescence decay from the 597 nm peak consisted mainly of the long ~123 μ s decay with 99.5% intensity fraction, whereas that from the 441 nm lacked the microsecond decay components but with lifetime components very similar to the three resolved short lifetime components of the total intensity decay of ZnS:Mn from both emission peaks. Figure 6 shows the reconstructed time-domain decay profiles of both coated LaF₃:Ce,Tb and ZnS:Mn. The total intensities of both samples were normalized to facilitate the comparison. It is clear that the ZnS:Mn exhibited a longer decay with appreciable intensity up to 300 μ s, and the intensity of the LaF₃: Ce,Tb became negligible after 200 μ s.

Finally, a similar multicomponent decay analysis was performed on the surface-bound nanoparticles on different substrates (quartz, aluminum and polymethylpentene plastic) in the air-dried state, and the results are summarized in Table 4. The surface labeling procedure here was identical to that for the fingerprint imaging. The quartz substrate used in this study had a negligible fluorescence background, and the labeled fingerprints on it were of quality similar to those on a glass surface (results not shown). For the surface-bound LaF₃:Ce,Tb, the resolved long decay lifetimes (τ_1) were ~14, 35, and 19 μ s, with intensity fractions of ~25, 46, and 5% for quartz, aluminum and plastic substrates, respectively. For the plastic substrate, the two resolved short-lifetime decays (τ_3 and τ_4 of ~2 and 1 ns, respectively) made up ~87% of the total intensity, as compared with the only ~50 or 13% total intensity for the quartz or aluminum substrate, respectively.

For the surface-bound ZnS:Mn nanoparticles, the resolved long decay lifetimes (τ_1) were ~72, 50, and 86 μ s with intensity fractions of ~80, 60, and 12% for quartz, aluminum, and plastic substrates, respectively, as shown in Table 4. For the plastic substrate, the two short lifetimes (τ_3 and τ_4 of ~2 and 0.01 ns, respectively) made up ~80% of the total intensity as compared with the much smaller ~10% total intensity for the quartz or aluminum substrate, respectively. This observation was similar to that for the surface-bound La₃:Ce,Tb nanoparticles on plastic, as described above. Figure 7A and B demonstrates the representative frequency-domain data of the surface-bound ZnS:Mn nanoparticles on quartz and plastic substrates, which exhibited low and high fluorescence background, respectively. The large differences in the modulation and phase difference data for the two substrates were further reflected in the large disparity in the recovered intensity fractions of the short lifetimes, particularly β_3 , as well as in the average lifetime of ~59 μ s (quartz) versus 11 μ s (plastic), as summarized in Table 4.

Since the short lifetime decays (0–2 ns) represented the major intensity components of the surface-bound nanoparticles on a plastic substrate, the fluorescence decay parameters from the plastic substrate itself were also determined as an important control. A major decay lifetime (τ_3) of 1.62 ns of ~70% intensity was clearly observed, as shown in Table 4. This short lifetime intensity fraction was very similar to that found in the surface-bounded ZnS:Mn on plastic, indicating that the main contribution of intensity decay for the surface-bound ZnS:Mn on plastic was from the substrate. Similar to Figure 6, the time domain decay behavior of the above is demonstrated in Figure 7C. It is clear that the fluorescence intensity of plastic (control) became negligibly small, but an appreciable intensity was evident for the surface-bound ZnS:Mn on plastic and quartz after 50 μ s.

Discussion

Our HRTEM measurements^{10,19} revealed that the sizes of our coated LaF₃:Ce,Tb and ZnS:Mn nanoparticles were ~20 and 5 nm, respectively. These values agree favorably with the size estimations based on the exciton peak locations and previous XRD measurements on similar nanoparticles.^{10,19} Both types of nanoparticles exhibited excellent potential for trace biomaterials detections on a surface, as demonstrated by the well-resolved individual sweat pores of the fingerprint images on aluminum and polymethylpentene plastic substrates.

The prominent fluorescence excitation peak at 270 nm for the COOH-PEG-COOH-coated LaF₃:Ce,Tb nanoparticles came from the strong 4f-5d absorption band of the doped Ce³⁺ ions.¹⁶ In addition, several weaker and longer wavelength peaks at 344, 354, 372, and 380 nm were likely due to the UV excitation bands corresponding to the transitions from the ⁷F₆ state to the other higher energy states of the doped Tb³⁺ ions. Note that the observation of same peaks in LaF₃:Tb but in the absence of Ce³⁺ ions¹⁵ supported the above peak assignments. The four emission peaks at 487, 540, 584, and 622 nm of the COOH-PEG-COOH-coated LaF₃:Ce,Tb nanoparticles corresponded to the strong and typical ⁵D₄-to-⁷F_J ($J = 6 - 3$) transitions of the doped Tb³⁺,¹⁶ whereas the rather weak and shorter wavelength emission peaks (334 and 363 nm) are likely from the doped Ce³⁺ emission¹⁶ and the self-trapped exciton emission from the LaF₃ host.¹⁹ The observation of a weak Ce³⁺ emission but a prominent excitation from Ce³⁺ indicates the presence of an efficient energy transfer from the doped Ce³⁺ (donor) to the Tb³⁺ (acceptor) ions within the lattice host of LaF₃ in COOH-PEG-COOH-coated LaF₃:Ce,Tb nanoparticles.^{14,19} The above spectral signature (Table 1) strongly indicates the presence of doped Ce³⁺ and Tb³⁺ that were incorporated into the LaF₃ host lattice in our surface-functionalized nanoparticles.

For the TGA-coated ZnS:Mn nanoparticles, the prominent fluorescence excitation peak at 283 nm was due to the band-to-band transition of the host ZnS.¹⁰ The two emission peaks at 441 and 597 nm were associated with the recombination of free charge carriers at the defect sites from ZnS¹³ and the ⁴T₁-to-⁶A₁ transition of the doped Mn²⁺ ions,¹⁰ respectively. These spectral features suggest the presence of appropriately doped Mn²⁺ in our nanoparticles and that the luminescence properties of ZnS:Mn depend on both the energy states of the ZnS host and the doped Mn²⁺ ions.

Upon excitation, the fluorescence intensity decays of both nanoparticles exhibit complex, multiexponential decay behavior. The resolved fluorescence decay lifetimes arise from several origins. Usually, the short lifetime decay is attributable to the exciton, or band-edge emission, an intrinsic semiconductor electron-hole pair recombination process.^{2,3,22} The longer lifetime decay is associated with traps usually located at and near the nanocrystal surface.²² As the nanoparticle size decreases, the surface-to-volume ratio increases. In addition, the introduction of the surface functionalization will influence the surface states and the solvent exposure of the particles. Therefore, the observed long decay lifetime component of the nanoparticles should depend strongly on the size, surface functionalization, and solvent exposure of the particles, in addition to other factors, such as temperature, wavelength of emission, and excitation energy.^{1-3,22}

The interpretation of the fluorescence decays from doped nanoparticles is more complicated than from the undoped nanoparticles. Other than the presence of the trap states on the surface of the crystals, the locations of the doped ions, which also participate in the luminescence process, are also important. For the case of the COOH-PEG-COOH-coated La₃:Ce,Tb nanoparticles, the photon energy absorbed by the doped Ce³⁺ ions may also transfer to the adjacent doped Tb³⁺ ions within the LaF₃ host matrix.¹⁰ The emission from the directly excited Ce³⁺ ions and that from the self-trapped exciton emission LaF₃ host in the short wavelength

region (300–400 nm) was quite weak when compared to the prominent green emission of Tb^{3+} , as demonstrated in this study. Previous fluorescence decay studies in Tb^{3+} -doped LaF_3 nanocrystals have indicated the presence of multiple decay components consisting of millisecond and shorter lifetimes.^{15,19} The longest component (3–4 ms) was found to be independent of the wavelength and capping of the nanoparticles, indicating that the longest millisecond component arises from the doped Tb^{3+} ions inside the nanocrystals and away from the surface or defect states.¹⁹ Therefore, we conclude that the microsecond and shorter lifetime components we measured were associated with the doped Tb^{3+} ions at or near the surface that are sensitive to the solvent and stabilizing groups for surface functionalization.

For the case of the TGA-coated ZnS:Mn nanoparticles, the observed 441 and 597 nm fluorescence peaks were related to the emitters from the ZnS lattice host and the doped Mn^{2+} ions, respectively. Their decay dynamics were separately examined. The fluorescence decay from the 441 nm peak had three major components, ~170 ns (50%), 10 ns (30%) and 1 ns (20%), whereas that from the 597 nm peak showed a major lifetime component at ~120 μs . Therefore, the total emission decay from the coated ZnS:Mn involves the long decay component from Mn^{2+} at 597 nm and the short decay component from ZnS at a well-separated wavelength of 441 nm. As a fluorescence labeling agent, these coated ZnS:Mn nanoparticles offer a unique advantage over other conventional labeling agents by allowing us to select the short or long-decay fluorescence signal by simply selecting the 441 or 597 nm peak, respectively.

Since we are primarily interested in exploring the potential of microsecond decay labels for detection of trace biomaterials on forensic relevant surfaces, the decay behavior of the coated $\text{LaF}_3\text{:Ce,Tb}$ and ZnS:Mn on air-dried solid substrates was also examined. As the surface-bound and labeled nanoparticles migrated to the air-dried state, a decrease in the decay lifetimes, especially the longest component, for both coated $\text{LaF}_3\text{:Ce,Tb}$ and ZnS:Mn was evident. The results suggest that the air-drying process significantly altered the surface states of the nanocrystals. Although the solvent interaction with the surface states was eliminated, new interactions of the stabilizing agents, COOH-PEG-COOH and TGA in our case, with the nanoparticle surface created different trap states. These new interactions might enhance the rate of nonradiative relaxation and give rise to luminescence quenching.¹⁹ In addition, the potential aggregation of the nanoparticles due to the breakdown of the stabilizing agents in the dried state might also contribute to the decrease in decay lifetime. Using the average lifetime to rank the degree of quenching, the order of quenching for the $\text{COOH-PEG-COOH-La}_3\text{:Ce,Tb}$ nanoparticles on different substrates is plastic > quartz > aluminum. The order for the TGA- Zn:Mn is plastic > aluminum > quartz. The highest quenching observed for both nanoparticles on plastic was related to the presence of strong background fluorescence from the substrate. In addition, the hydrophobic surface of the plastic might strongly promote self-aggregation of the water-soluble nanoparticles that effectively quenched the fluorescence decay.

This study provides useful information in assessing the potential of using surface-functionalized nanoparticles as fluorescence labeling agents for future nanoforensic applications. For trace evidence detections on surfaces in forensic applications, the presence of a high fluorescence background is a major obstacle in revealing the targeted biomaterials. Here, the availability of the microsecond decay labeling agents, that is, surface functionalized nanoparticles, in the dried state represents a milestone in the emerging field of nanoforensic science. Note that the use of a time-gated fluorescence detection method has been demonstrated for background suppression in biological cell imaging⁵ and cyanoacrylate-polymerized fingerprint detection,⁴ which involved nanosecond-decay quantum dots and a phosphorescence dye, respectively. The general approach of this method is to excite the samples with a pulsed light source and collect the images after a certain time delay. At the time

of image collection, the strong and short-lived emission from the background can be effectively suppressed (background suppression), and the intensity from the long-lived labels can be collected. Obviously, the choice of the time delay and the extent of background suppression depend on the difference in the decay lifetimes of the labels and that of the background. The decay lifetimes of most forensically relevant surfaces are in the nanosecond regime;^{4,8-9} for example, 360 ns for the highly fluorescent polymethylpentene plastic in this study. In our case, a microsecond delay is an ideal delay time window for the time-gated detection by using our nanoparticles as the labeling agents. Note that the background-suppressed detection can also be operated in the frequency domain⁴⁰ using the modulation frequency in the kilohertz region.

Our surface-functionalized and long-decay nanoparticles directly labeled the protein residues of the target biomaterials without chemical fuming, for example, cyanoacrylate polymerization,⁴ which would destroy the chemical specificity of the target materials on the surface before the fluorescence labeling. The incorporation of drug- or metabolite-specific antibodies³² to the surface of our water-soluble nanoparticles will further enhance the chemical- and biospecific targeting capability of our nanoparticles for future nanoforensic applications on surfaces with high fluorescence background.

The fluorescence decay of our nanoparticles offers an additional fluorescence parameter, other than wavelength and intensity, for detection of trace biomaterials on surfaces. The coated ZnS:Mn nanoparticles exhibited a longer average decay lifetime (130 μ s) when compared with the coated LaF₃:Ce,Tb nanoparticles (24 μ s) in solution. Most importantly, the decay lifetimes of the surface-bound ZnS:Mn ranging from 11 to 60 μ s were significantly longer than that of the surface-bound LaF₃:Ce,Tb (1–16 μ s). In addition, the relative nontoxic and environmentally friendly nature of the compounds in ZnS:Mn²⁺ when compared to La₃:Ce,Tb would make the coated ZnS:Mn nanoparticles a better fluorescence labeling agent for the future ultrasensitive, background-suppressed detections of trace biomaterials on surfaces.

Conclusion

In summary, we have examined the decay dynamics and potential for detection of trace biomaterials of two water-soluble and surface-functionalized nanoparticles, COOH-PEG-COOH-coated LaF₃:Ce,Tb and TGA-coated ZnS:Mn. Both nanoparticles exhibited microsecond decay lifetime in solution. Upon binding to fingerprint residues and in the dried state, the surface-bound ZnS:Mn particles retained the microsecond decay properties for all substrates, aluminum, glass, quartz, and plastic. Therefore, the coated ZnS:Mn nanoparticles hold great promise as a nontoxic, fluorescence labeling agent for future ultrasensitive, background-suppressed trace evidence detections in nanoforensic applications.

Acknowledgments

This work was supported by the Robert A. Welch Research Foundation (D-1158) and the U.S. Department of Justice, National Institute of Justice (2003-IJ-CX-K016). W. Chen is grateful for financial support from the Startup and LERR Funds from University of Texas at Arlington, TX, the NSF and DHS joint program (CBET-0736172), DOD HDTRA1-08-P-0034 and the DOD Congressionally Directed Medical Research Programs (W81XWH-08-1-0450).

References and Notes

1. Yu WW, Chang E, Drezek R, Colvin VL. *J. Phys. Chem. B* 2006;348:781–786.
2. Chen W. *J. Nanosci. Nanotechnol* 2008;8:1019–1051. [PubMed: 18468106]
3. Burda C, Chen XB, Narayanan R, El-Sayed MA. *Chem. Rev* 2005;105:1025–1102. [PubMed: 15826010]
4. Roorda RD, Ribes AC, Damaskinos S, Dixon AE, Menzel ER. *J. Forensic Sci* 2000;45:563–567. [PubMed: 10855959]

5. Dahan M, Laurence T, Pinaud F, Chemla DS, Alivisatos AP, Sauer M, Weiss S. *Opt. Lett* 2001;26:825–827. [PubMed: 18040463]
6. Liu L, Gill SK, Gao YP, Hope-Weeks LJ, Cheng KH. *Forensic Sci. Int* 2008;176:163–172. [PubMed: 17913419]
7. Menzel ER. *Sci. World J* 2001;1:498–509.
8. Menzel ER, Savoy SM, Ulvick SJ, Cheng KH, Murdock RH, Sudduth MR. *J. Forensic Sci* 2000;45:545–551. [PubMed: 10855957]
9. Menzel ER, Takatsu M, Murdock RH, Bouldin K, Cheng KH. *J. Forensic Sci* 2000;45:770–773. [PubMed: 10914569]
10. Chen W, Aguekian VF, Vassiliev N, Serov AY, Filosofov NG. *J. Chem. Phys* 2005;123:1–5.
11. Borse PH, Srinivas D, Shinde RF, Date SK, Vogel W, Kulkarni SK. *Phys. Rev. B* 1999;60:8659–8664.
12. Bol AA, Meijerink A. *Phys. Rev. B* 1998;58:R15997.
13. Bhatti HS, Sharma R, Verma NK, Kumar N, Vadera SR, Manzoor K. *J. Phys. D: Appl. Phys* 2006;39:1754–1760.
14. Yu LX, Song HW, Liu ZX, Yang LM, Zheng SLZ. *J. Phys. Chem. B* 2005;109:11450–11455. [PubMed: 16852401]
15. Wang JS, Bo SH, Song LM, Hu J, Liu XH, Zhen Z. *Nanotechnology* 2007;18:1–6.
16. Wang F, Zhang Y, Fan XP, Wang MQ. *J. Mater. Chem* 2006;16:1031–1034.
17. Smith BA, Zhang JZ, Joly A, Liu J. *Phys. Rev. B* 2000;62:2021.
18. Moses WW, Derenzo SE, Weber MJ, Raychaudhuri AK, Cerrina F. *J. Lumin* 1994;59:89–100.
19. Liu YF, Chen W, Wang SP, Joly AG, Westcott S, Woo BK. *J. Appl. Phys* 2008;103:1–7.
20. Lis S. *J. Alloys Compd* 2002;341:45–50.
21. Alivisatos P. *Nat. Biotechnol* 2004;22:47–52. [PubMed: 14704706]
22. Brus LE. *J. Chem. Phys* 1984;80:4403–4409.
23. Steigerwald ML, Brus LE. *Acc. Chem. Res* 1990;23:183–188.
24. Oneil M, Marohn J, McLendon G. *Chem. Phys. Lett* 1990;168:208–210.
25. Oneil M, Marohn J, McLendon G. *J. Phys. Chem* 1990;94:4356–4363.
26. Lakowicz JR, Gryczynski I, Piszczek G, Murphy CJ. *J. Phys. Chem. B* 2002;106:5365–5370.
27. Lakowicz JR, Gryczynski I, Gryczynski Z, Murphy CJ. *J. Phys. Chem. B* 1999;103:7613–7620.
28. Cheng KH. *Biophys. J* 1989;55:1025–1031. [PubMed: 2765643]
29. Spencer RD, Weber G. *J. Chem. Phys* 1970;52:1654–1663.
30. Gratton E, Jameson DM, Hall RD. *Annu. Rev. Biophys. Bioeng* 1984;13:105–124. [PubMed: 6378065]
31. Cheng KH, Ajimo J, Chen W. *J. Nanosci. Nanotechnol* 2008;8:1170–1173. [PubMed: 18468118]
32. Leggett R, Lee-Smith EE, Jickells SM, Russell DA. *Angew. Chem., Int. Ed* 2007;46:4100–4103.
33. Abramoff MD, Magelhaes PJ, Ram SJ. *Biophotonics Int* 2004;11:36–42.
34. Yanes AC, Del-Castillo J, Mèndez-Ramos J, Rodríguez VD, Torres ME, Arbiol J. *Opt. Mater* 2007;29:999–1003.
35. Chen W, Su F, Li G, Joly AG, Malm J-O, Bovin J-O. *J. Appl. Phys* 2002;92:1950–1955.
36. Chen W, Malm J-O, Zwiller V, Wallenberg R, Bovin J-O. *J. Appl. Phys* 2001;89:2671–2675.
37. Cannon B, Heath G, Huang JY, Somerharju P, Virtanen JA, Cheng KH. *Biophys. J* 2003;84:3777–3791. [PubMed: 12770884]
38. Llanos J, Castillo R, Alvarez W. *Mater. Lett* 2008;62:3597–3599.
39. Khaidukov NM, Lam SK, Lo D, Makhov VN. *Opt. Commun* 2002;205:415–420.
40. Menzel ER, Popovic ZD. *Rev. Sci. Instrum* 1978;49:39–44.

Figure 1.

Schematic diagram of a surface-functionalized nanoparticle (X-NP). Here, X represents the surface chemical group, COOH-PEG-COOH or TGA. The nanoparticle core (NP) is $\text{LaF}_3\text{:Ce,Tb}$ or ZnS:Mn . Each X chemical group has one carboxylic ($-\text{COOH}$) functional subgroup in its chemical structure.

Figure 2. Representative HRTEM images of LaF₃,Ce,Tb (A) and TGA-ZnS:Mn nanoparticles. The scale bars are also shown.

Figure 3.

UV-visible absorption (black solid line), fluorescence excitation (black dashed line), and fluorescence emission (red line) spectra of coated $\text{LaF}_3\text{:Ce,Tb}$ (A) and ZnS:Mn nanoparticles (B). The fluorescence excitation and emission spectra of a polymethylpentene plastic sheet (C) is also shown. The insert in either panel A or B represents the first-order derivative spectrum of the absorbance with vertical bars in the insert indicating the dip and peak. The location of the exciton peak (arrow) is defined as the midpoint between the dip and peak of the above derivative spectrum. For the coated $\text{LaF}_3\text{:Ce,Tb}$ nanoparticles in panel A, the fluorescence emission was at 550 nm for the excitation spectrum, and the excitation wavelength was at 275 nm for the emission spectrum. The corresponding wavelengths were 580 and 330 nm for the

coated ZnS:Mn nanoparticles in panel B, and 400 and 325 nm for the plastic in panel C. All spectra were collected at room temperature.

Figure 4. Representative fluorescence images of latent fingerprints labeled by coated LaF₃:Ce,Tb (A–C) and ZnS:Mn (D–F) on aluminum (A, D), glass (B, E) and polymethylpentene plastic (C, F) surfaces in the air-dried state and at room temperature. The scale bars indicate 2 mm. See Materials and Methods for imaging conditions.

Figure 5.

The heterogeneous decay behavior of coated $\text{LaF}_3:\text{Ce,Tb}$ in solution is demonstrated by the use of multiexponential decay fits (1-component (a), 2-component (b), 3-component (c) and 4-component (dashed line)) to the frequency domain demodulation (A) and phase difference (B) data. The representative fluorescence decay parameters are shown in Table 2. The excitation was at 325 nm, and the fluorescence emission was collected with a 350 nm long-pass filter.

Figure 6.

Comparisons of reconstructed fluorescence intensity decays of the coated $\text{LaF}_3\text{:Ce,Tb}$ (line a) and ZnS:Mn (line b) in solution and at room temperature. To facilitate comparisons, the total fluorescence intensity of each decay curve was normalized. The excitation was at 325 nm, and the fluorescence emission was collected with a 350 nm long-pass filter.

Figure 7.

The frequency domain demodulation (A) and phase difference (B) data of coated ZnS:Mn on a quartz plate (open triangle) and a polymethylpentene plastic plate (open circle) and of a polymethylpentene plastic plate without nanoparticles (closed circle) are shown. The lines (solid for nanoparticles and dashed for plastic) in panels A and B indicate the four-component exponential decay fits to the frequency domain data. The representative fluorescence decay parameters of the fits are shown in Table 4. On the basis of the fitted decay parameters, time domain fluorescence intensity decay data (C) were generated for the plastic control (line a), and the surface-bound ZnS:Mn on plastic (line b) and quartz (line c) plates.

TABLE 1

Spectral Characterizations of Surface-Functionalized Nanoparticles in Solution^a

Sample	exciton peak (nm)	excitation peaks (nm)	assignments	emission peaks (nm)	assignment
LaF ₃ Ce, Tb	307	276	² F _{5/2} - ⁵ d ¹ (Ce ³⁺)	334	⁵ d ¹ - ² F _{5/2} (Ce ³⁺)
		344	⁷ F ₆ - ⁵ L ₆ (Tb ³⁺)	363	⁵ d ¹ - ² F _{7/2} (Ce ³⁺)
		354	⁷ F ₆ - ⁵ L ₉ (Tb ³⁺)	487	⁵ D ₄ - ⁷ F ₆ (Tb ³⁺)
		372	⁷ F ₆ - ⁵ G ₆ (Tb ³⁺)	540	⁵ D ₄ - ⁷ F ₅ (Tb ³⁺)
		380	⁷ F ₆ - ⁵ G ₆ (Tb ³⁺)	584	⁵ D ₄ - ⁷ F ₄ (Tb ³⁺)
ZnS:Mn	283			622	⁵ D ₄ - ⁷ F ₃ (Tb ³⁺)
				441	D-A pairs
				597	⁴ T ₁ - ⁶ A ₁ (Mn ²⁺)

^aThe measured spectral parameters of different nanoparticles are shown. The exciton peak was obtained from the first-order derivative spectrum of the UV-visible absorption spectra (see Figure 2 and Materials and Methods). The excitation and emission peaks were obtained from the fluorescence excitation and emission spectra as given in Figure 3. For the spectra involving multiple peaks, the major peak is highlighted in bold. The spectral assignments of the peaks are also shown.

TABLE 2
Heterogeneous Decay Characteristics of the COOH-PEG-COOH-Coated LaF₃Ce:Tb Nanoparticles in Solution^a

τ_1 (ns)	β_1	τ_2 (ns)	β_2	τ_3 (ns)	β_3	τ_4 (ns)	β_4	τ_{av} (ns)	χ^2
2.06 (0.01)	1.0							2.06 (0.01)	887.5
13.62 (0.14)	0.507 (0.002)	1.19 (0.01)	0.493					7.49 (0.10)	199.9
54.47 (1.41)	0.249 (0.002)	5.05 (0.09)	0.165 (0.002)	0.73 (0.02)	0.292			14.61 (0.49)	115.3
67849 (16096)	0.353 (0.005)	35.47 (1.08)	0.167 (0.004)	4.33 (0.10)	0.302 (0.004)	0.657 (0.020)	0.227	23958 (6022)	2.9

^aThe complex, heterogeneous decay behavior is demonstrated by the multiple-exponential decay fits to the frequency domain data (see Materials and Methods). The recovered fluorescence decay parameters (τ_i 's and β_i 's) and their uncertainties (in parentheses) are shown. The intensity-averaged fluorescence lifetime (τ_{av}) and the χ^2 values of different fits are shown.

TABLE 3
Fluorescence Decay Parameters of TGA Coated ZnS:Mn Nanoparticles in Solution^a

sample	τ_1 (μ s)	β_1	τ_2 (ns)	β_2	τ_3 (ns)	β_3	τ_4 (ns)	β_4	τ_{av} (μ s)
ZnS:Mn (>350 nm)	132.09 (32.31)	0.971 (0.002)	141.3 (2.9)	0.011 (0.003)	13.33 (0.25)	0.009 (0.002)	1.067 (0.010)	0.009	129.26 (31.63)
ZnS:Mn (>530 nm)	122.98 (14.14)	0.995 (0.002)	154.84 (1.23)	0.004 (0.002)	2.54 (0.01)	0.002 (0.002)			122.36 (14.32)
ZnS:Mn (400–500 nm)			167.57 (1.47)	0.522 (0.002)	8.61 (0.09)	0.303 (0.002)	0.643 (0.008)	0.175	0.091 (0.001)

^aThe recovered fluorescence decay parameters (τ_i 's and β_i 's) and their uncertainties (in parentheses) of functionalized nanoparticles in solution are shown. The intensity-averaged fluorescence lifetime, τ_{av} is also shown.

Fluorescence Decay Parameters of Surface-Bound COOH-PEG-COOH Coated LaF₃Ce,Tb and TGA-Coated ZnS:Mn Nanoparticles on Different Substrates in the Air-Dried State^a

TABLE 4

sample	$\tau_1(\mu s)$	B_1	$\tau_2(ns)$	B_2	$\tau_3(ns)$	B_3	$\tau_4(ns)$	B_4	$\tau_{av}(\mu s)$
LaF ₃ Ce,Tb (quartz)	13.80 (2.07)	0.245(0.004)	39.38 (0.91)	0.262 (0.004)	5.31 (0.14)	0.291 (0.004)	0.909 (0.019)	0.202	3.39 (0.56)
LaF ₃ Ce,Tb (aluminum)	35.28 (5.06)	0.455 (0.002)	34.37 (0.21)	0.410 (0.005)	3.25 (0.02)	0.134 (0.002)	2.33 (0.03)	0.001	16.07 (2.37)
LaF ₃ Ce,Tb (plastic)	19.04 (5.03)	0.045 (0.005)	28.39 (2.86)	0.073 (0.005)	2.25 (0.17)	0.427 (0.047)	0.705 (0.057)	0.455	0.86 (3.21)
ZnS:Mn (quartz)	72.23 (5.34)	0.81 (0.002)	60.23 (0.76)	0.098 (0.003)	6.80 (0.13)	0.051 (0.002)	0.603 (0.010)	0.038	58.73 (4.48)
ZnS:Mn (aluminum)	50.00 (5.56)	0.612 (0.002)	38.93 (0.36)	0.242 (0.004)	4.59 (0.04)	0.126 (0.002)	0.005 (0.002)	0.018	30.61 (3.50)
ZnS:Mn (plastic)	86.36 (6.46)	0.124 (0.002)	26.50 (1.78)	0.083 (0.003)	1.73 (0.02)	0.649 (0.005)	0.005 (0.002)	0.145	10.71 (0.97)
* plasticonly	7.69 (4.22)	0.046 (0.002)	25.36 (1.37)	0.120 (0.004)	1.62 (0.07)	0.685 (0.048)	0.192 (0.241)	0.149	0.36 (0.21)

^aThe recovered fluorescence decay parameters (τ_i 's and β_i 's) and their uncertainties (in parentheses) of different functionalized nanoparticles in the air-dried state are shown. The intensity-averaged fluorescence lifetime, τ_{av} , is also shown.

(*) The decay parameters from the polymethylpentene plastic surface in the absence of nanoparticles are also shown.