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Photoluminescent CdS/Dendrimer Nanocomposites for Fingerprint Detection

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ABSTRACT: CdS/dendrimer nanocomposites with a range of concentrations of the photoluminescent semiconductor nanocluster and the dendrimer are prepared in methanol and 1:9 methanol:water solutions. The solutions are utilized for detection of cyanoacrylate ester fumed and unfumed fingerprints on polyethylene and aluminum foil.

KEYWORDS: forensic science, fingerprints, photoluminescence, semiconductor nanocrystal, cadmium sulfide, dendrimer, nanocomposite, time-resolved imaging

The photoluminescence detection of latent fingerprints has in the last 20 years become a very successful methodology. However, there are still all too many items that defy processing because of intense background fluorescence from the article itself. Thus, time-resolved approaches involving gated (time-domain) and phase-resolved (frequency-domain) imaging are being explored to permit background suppression. From the instrumentation perspective, gated imaging is mature. Although photoluminescence lifetimes of microsecond order and even shorter are amenable in principle to gated fingerprint imaging, practicality considerations generally call for lifetimes of millisecond order (1). The pertinent fingerprint treatments, largely involving a lanthanide-based strategy that mostly utilizes europium complexes, leave much to be desired for detection on porous surfaces of fingerprints that are not fresh, however. Phase-resolved imaging systems have been operational for some time in cell microscopy, for instance, and instruments for fingerprint work are under development. These systems are suitable for photoluminescence lifetimes of nanosecond order, but the needed companion fingerprint treatment strategy has yet to be developed. Recently, a suitable and potentially universal approach involving photoluminescent semiconductor nanocrystals was sug-

gested (1). Its feasibility has been demonstrated (2–4), including the concept of selective fingerprint tagging with dendrimers. Apart from photoluminescence lifetimes compatible with phase-resolved imaging and even gated imaging, the salient virtues of photoluminescent semiconductor nanocrystals (such as CdS or CdSe), referred to also as nanocrystallites, nanoparticles, nanoclusters, or quantum dots, are tunability of excitation and emission wavelengths by tailoring of nanocrystal size, high photoluminescence efficiency, robustness, encapsulation with flexibility of functionalization with conjugating ligands for selective labeling of fingerprints. The combination of nanocrystals and dendrimers to form photoluminescent nanocomposites suitable for fingerprint detection was recently taken up in preliminary study as well (3,4), with CdS/Starburst[®] dendrimer nanocomposites in particular. A number of issues that arise in connection with their use on fingerprints are the focus of this article, including dendrimer size, absolute and relative CdS/dendrimer concentrations, solvent systems, photoluminescence spectra and lifetimes, fingerprint treatments and range of applicability. We predict that photoluminescent semiconductor nanocrystals/nanocomposites will form the next milestone in fingerprint detection methodology.

CdS/dendrimer Nanocomposite Preparation

Dendrimers have lately seen intense attention (5) in many areas of science, especially in connection with incorporation into them of nanoparticles for purposes of applications such as cancer drug delivery, catalysis, optical devices, waste clean-up, etc. Of particular interest is a photoluminescent nanocomposite of CdS with Starburst[®] (PAMAM) dendrimer that was first (outside the forensic science context) reported by Sooklal, Hanus, Ploehn, and Murphy (6). The dendrimer type we selected for the present study is functionalized with terminal amino groups. This selection was made because the amino groups can react with carboxylic acids (which are copiously found in fingerprint material) to form amide linkages, thus tagging the fingerprint. We examined Generation 0, 1, and 4 Starburst[®] (PAMAM) dendrimers (7), available commercially from Aldrich. They have 4, 8, and 64 terminal amino groups, respectively. As purchased, the dendrimers come in methanol solution. The preparation in methanol of the CdS/dendrimer nanocomposite simply involves diluting the dendrimer solution and adding to it, repetitively, in small quantities, equal volumes of equimolar methanol solutions of cadmium nitrate and sodium sulfide. It does not matter much whether the cadmium nitrate is added to the dendrimer solution first, followed by the sodium sulfide, whether the sequence is reversed or whether both are added simultaneously. Since we utilized small quantities of

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solution in our studies, sequential aliquot addition was employed, for convenience, with cadmium nitrate added to the dendrimer solution first. Repetitive additions (at room temperature) of cadmium nitrate and sodium sulfide typically used either 5 or 10 aliquots of each reagent. In addition to this methanol preparation of the CdS/dendrimer nanocomposite, we also studied a 10% methanol, 90% water formulation, which was prepared similarly, with the dendrimer methanol solution appropriately diluted with water and with the cadmium nitrate and sodium sulfide dissolved in 1:9 methanol:water mixture. When cadmium nitrate and sodium sulfide are combined, cadmium sulfide generally forms as a precipitate. In the presence of the dendrimer, however, a nanocomposite forms, in solution or suspension, depending on concentrations, involving nanoclusters of cadmium sulfide molecules bound to dendrimer molecules or to aggregates of dendrimer molecules (6).

Concentrations

In the present study, we were primarily interested in physical fingerprint treatments akin to dye staining. Thus, our sample base was made up of bare and cyanoacrylate ester-fumed fingerprints (fresh to one-day-old) on aluminum foil and Ziploc® (polyethylene) sandwich bags. When such samples were initially dipped in CdS/dendrimer (Generation 4) methanol solutions that had dendrimer concentrations greater than about 10^{-4} M, the solutions were found to be rather tacky, such that too much background was formed by indiscriminate nanocomposite deposition, rather than selective adherence to fingerprints. Thus, we settled on dendrimer concentrations between 2 and 8×10^{-5} M in all subsequent methanol and 1:9 methanol:water preparations.

For a given Generation 4 dendrimer concentration in methanol, the observed luminescence was generally blue-green regardless of the CdS concentration in the nanocomposite, but the luminescence intensity increased with CdS concentration. For dendrimer concentration of 2×10^{-5} M, immediate precipitation occurred with CdS concentrations substantially larger than about 2×10^{-3} M. At about 2×10^{-3} M, precipitation occurred in time spans of about two days. Thus, we settled on optimal CdS/Generation 4 dendrimer concentrations in methanol of 8×10^{-4} M/ 2×10^{-5} M, which form solutions that are stable at room temperature for several days at least. The situation is rather different for 1:9 methanol:water. Here, the observed luminescence was generally yellow-orange. Precipitation occurred for CdS concentrations greater than about 8×10^{-4} M, regardless of dendrimer concentration. Optimal CdS/Generation 4 dendrimer concentration was 2×10^{-4} M/ 8×10^{-5} M. We examined in 1:9 methanol:water solution nanocomposite formation also with Generation 0 and 1 dendrimer. No useful preparations could be made; precipitation prevailed in all cases. With methanol solutions, nanocomposites could be formed with Generation 0 and 1 dendrimer, but they were not as good as those with Generation 4 dendrimer, in terms of luminescence intensity obtained from fingerprints. Mostly this was due to the necessity to keep CdS concentrations low to prevent precipitation. Evidently, the number of terminal amino groups dictates the tolerable concentration of CdS. The observation that photoluminescence color was basically invariant within each of the two solvent systems (barring precipitation), regardless of CdS concentration, and, for that matter, dendrimer concentration, indicates that nanocluster size is essentially constant, with nanocluster concentration varying. The optimizations given above were determined on the basis of solution luminescence intensity (with solution stability demanded as well)

and also intensity of fingerprint development. The two criteria paralleled each other.

Nanocomposite Spectroscopy

Absorption spectra were obtained for representative CdS/Generation 4 dendrimer solutions in methanol and 1:9 methanol:water. These are shown in Fig. 1 (7×10^{-4} M/ 4×10^{-5} M and 7×10^{-4} M/ 8×10^{-5} M, respectively). Comparison with literature absorption spectra (8) indicates CdS nanocluster sizes of roughly 2.5 and 3 nm, respectively. These sizes are significantly smaller than those of CdS capped with dioctyl sulfosuccinate (4), which we reported on earlier. That the fingerprint photoluminescence color in the methanol:water case is nonetheless orange (unusually far red-shifted), indicates the presence of Forster-type energy transfer (1). Excitation spectra yielded agreement with the absorption band-edges, i.e., luminescence drop-off at excitation wavelengths longer than about 360 and 390 nm for methanol and 1:9 methanol:water solutions, respectively.

Photoluminescence lifetime measurements utilized phase-resolved techniques. In both the methanol and 1:9 methanol:water cases, the (room temperature solution) luminescences were best interpreted by three-component fits. For the methanol case, the main component, with intensity fraction of about 0.6, had a lifetime of about 120 ns. The next component, with intensity fraction of about 0.3, had lifetime of about 30 ns and the third component a lifetime of about 3.5 ns. These values were reproducible over a range of CdS/dendrimer concentrations. For the 1:9 methanol:water case, the longest-lived component, with intensity fraction of about 0.35, had a lifetime of about 300 ns. The next component, with intensity

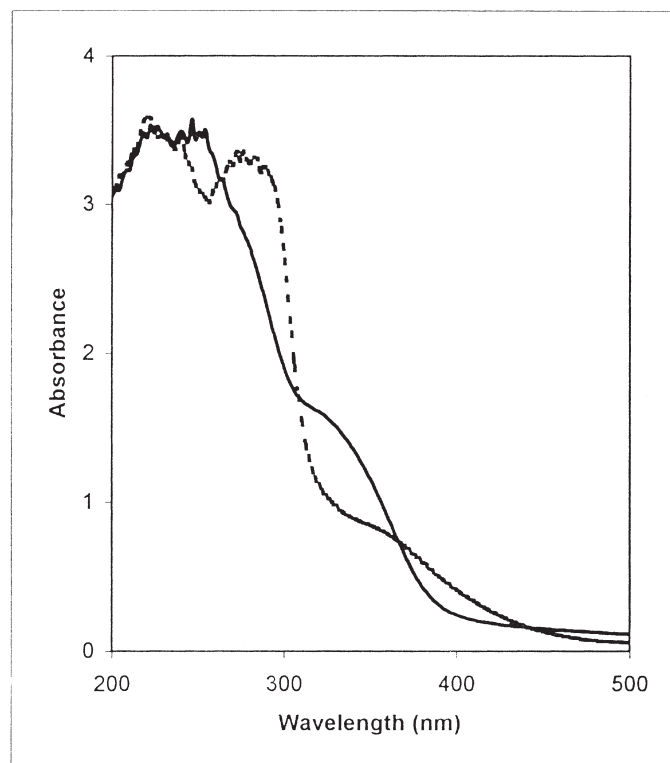


FIG. 1—Absorption spectra of CdS/Generation 4 Starburst®(PAMAM) dendrimer nanocomposite in methanol (solid spectrum) and in 1:9 methanol:water mixture (dashed spectrum).



FIG. 2—Cyanoacrylate ester-fumed fingerprint on aluminum foil, developed with CdS/dendrimer nanocomposite in methanol solution.

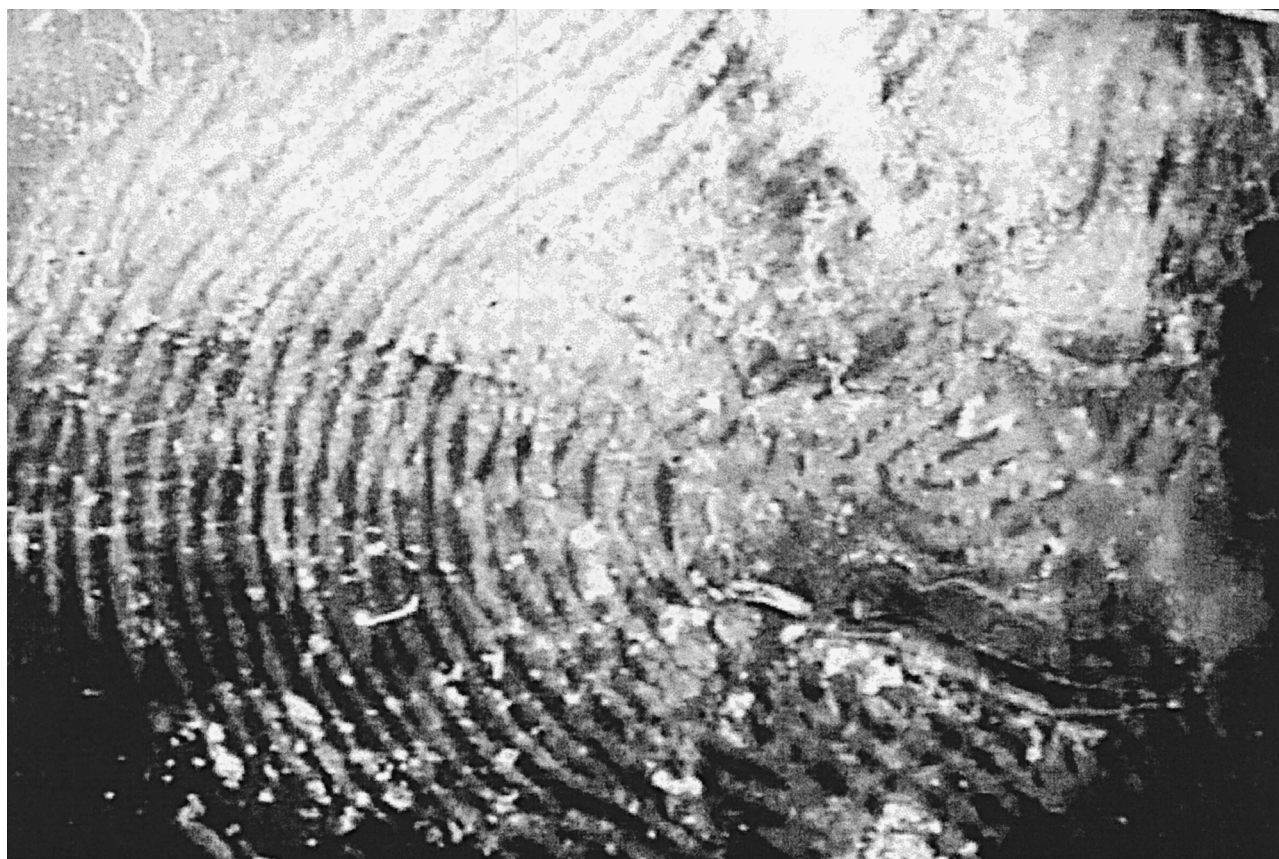


FIG. 3—Unfumed fingerprint on polyethylene, developed with CdS/dendrimer nanocomposite in 1:9 methanol:water solution.

fraction of about 0.45, had a lifetime of about 60 ns and the third component a lifetime of about 4.5 ns. Again, there was reproducibility over a range of CdS/dendrimer concentrations. Solution emission spectra showed broad luminescences peaked at about 480 nm (100 nm full width at half maximum) for methanol and 550 nm (130 nm fwhm) for 1:9 methanol:water.

Fingerprint Treatment

Fingerprint processing simply involved dipping the aluminum foil or polyethylene sample in the CdS/dendrimer solution and then letting dry completely. In customary fingerprint staining, such as with rhodamine 6G after cyanoacrylate ester fuming, the staining involves spraying the article or immersing it in the dye solution for a few seconds. Staining, in other words, is essentially instantaneous. With the CdS/dendrimer solutions, however, the immersion involved not seconds, but hours instead. Methanol solution dipping was not successful on unfumed fingerprints simply because the aggressive methanol solvent tended to wash away the fingerprints. Fumed prints, however, developed readily. An example print, photographed with a digital camera (Kodak DC 120) under near-ultraviolet excitation (about 50 mW) from an Ar-laser, is shown in Fig. 2. The methanol:water solvent system lent itself to fumed as well as unfumed prints. Dipped articles were typically left in solutions overnight before inspection. An example of thus developed prints, excited and photographed as above, is shown in Fig. 3. Adherence of the nanocomposite everywhere precluded detection of (unfumed) fingerprints on paper. The long dipping times suggest that reaction of the amino functionality of the dendrimers with carboxylic acid of the fingerprint residue or, for that matter, the cyanoacrylate polymer is perhaps occurring, forming amide bonds. This is a widely used general labeling strategy. However, OH is a poor leaving group. It

thus remains unclear at this time whether the fingerprint development is dominated by chemical or physical mechanisms. This should be resolved by an upcoming study of fingerprint detection that includes diimides to produce an intermediate ester from carboxylic acid in order to facilitate the subsequent formation of amide linkages. Nature already provides ester linkages in the form of triglycerides. Carboxylate functionalized dendrimer will be studied for tagging of amino acid/protein of fingerprints.

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