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Morphological Dependence of Fluorescence Emitted from PbS/PAMAM Dendrimer Nanocomposite

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Strong fluorescence from G4 PAMAM dendrimer was observed in PbS/PAMAM dendrimer nanocomposite, which significantly depended on its morphology.

Because of their unique structure and properties, poly(amido amine) (PAMAM) dendrimers have been extensively studied. Up to date, several approaches have taken advantage of the uniqueness of dendrimers as the organic blocks to construct dendrimer–nanoparticle composites.[1] Meanwhile, a peculiar phenomenon, where the weak fluorescence was emitted from PAMAM dendrimers, was observed by different groups.[2] In our previous work,[3] it was also found that different kinds of dendrimers with tertiary amine branching points could emit strong fluorescence by adjusting pH value. These observations are unexpected, because PAMAM dendrimer is a kind of organic molecules without traditional fluorophore.

Herein, a strong fluorescence emission from an OH-terminated fourth-generation (G4) PAMAM dendrimer in PbS/PAMAM dendrimer nanocomposite is reported. The positions of fluorescence bands were different from those of innate dendrimer. Furthermore, the fluorescence properties significantly depended on the morphologies of PbS/PAMAM dendrimer nanocomposite in the aging process.

In the present experiments, OH-terminated G4 PAMAM dendrimer was utilized as a stabilizer for preparing PbS nanoparticles. Dendrimer (10 wt % in methanol) was purchased from Aldrich and used without further modification. The suspension with lower reactant concentration was prepared by mixing 5 mL of Pb^{2+} solution (1 mM $Pb(NO_3)^2$ and 1 mM of dendrimer in methanol) and 5 cm^3 of S^{2-} solution (1 mM Na_2S and 1 mM dendrimer in methanol) under stirring at room temperature. The obtained suspensions were kept at room temperature and characterized by fluorometry and transmission electron microscopy at different time intervals.

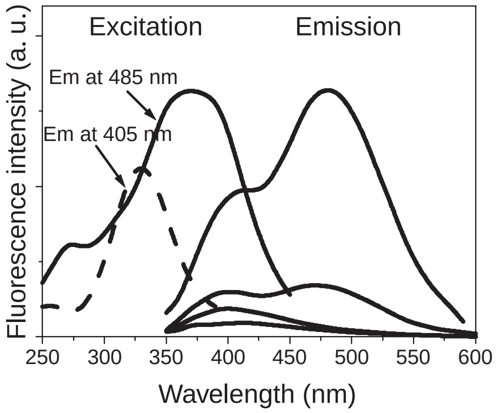

Figure 1. Fluorescence excitation and emission spectra of PbS/G4-PAMAM dendrimer nanocomposites. Left: excitation spectra at emission wavelengths of 405 and 485 nm at 15th day; right: emission spectra (excitation at 330 nm) at different aging times (1st, 5th, 8th, 15th day from bottom to top).

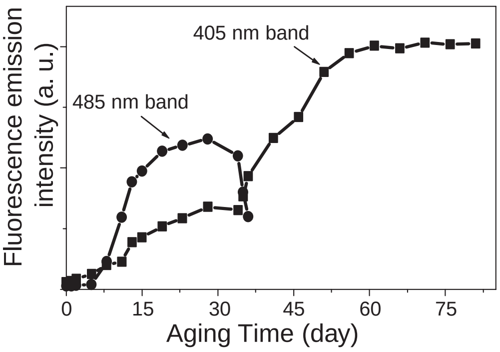

Figure 2. Aging time dependence of intensities of two emission bands upon excitation at 330 nm for PbS/G4-PAMAM dendrimer nanocomposite.

Figure 1 shows two fluorescence bands (405 and 485 nm) emitted from PbS/PAMAM dendrimer nanocomposite, whereas only a single emission band (450 nm) was observed in a PAMAM dendrimer solution as previously reported.[2,3] The corresponding excitation bands were at 330 and 375 nm. The intensities of the two emission bands varied in the process of aging, as seen in Figure 2. The intensity of the 405-nm-emission band increased gradually and reached a constant value after two months. Furthermore, it is rather remarkable that the 485-nm-emission band presented a maximum.

Figure 3 shows TEM images of PbS/PAMAM dendrimer nanocomposites at typical aging times. Well-defined PbS nanoparticles in the size dimension from 3 to 4 nm were fabricated just after the preparation of nanocomposite (Figure 3a). At the aging stage (20th day) with a strong 485-nm emission band, flocculation of PbS/PAMAM dendrimer nanocomposites occurred (Figure 3b). At this time, individual PbS nanoparticles could keep a distance from each other under the protection of PAMAM dendrimers. On the other hand, the nanocomposites were mutually attracted by van der Waals force. After further aging (45th and 60th day), the flocs of PbS/PAMAM dendrimer nanocomposites aggregated to large spherical assemblies, as detected by TEM (Figures 3c and 3d). Then the interparticle attractive force is far dominant over the repulsion, giving rise to coalescence, that is, secondary aggregation of PbS nanoparticles.

It is reported that semiconductive PbS nanoparticles can emit fluorescence, if they have suitable size and environments.[4]

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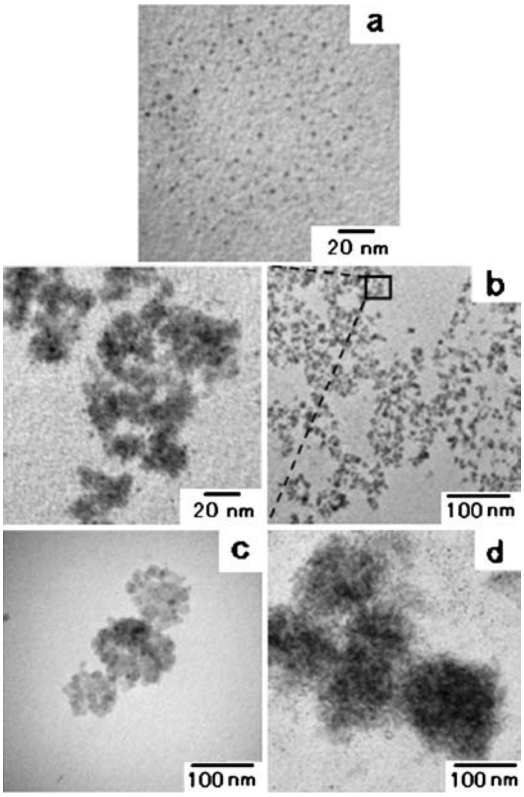

Figure 3. TEM images of PbS/G4-PAMAM dendrimer nanocomposites in the process of aging: (a) first day; (b) 20th day; (c) 45th day; (d) 60th day.

Nevertheless, it is assumed that two fluorescence emission bands observed in the present work are ascribed to G4 PAMAM dendrimer in the nanocomposite. This assumption was proposed on the basis of following reasons. Given that the fluorescence came from PbS nanoparticles, the intensities of fluorescence emission bands should be decreased with aging. Furthermore, the fluorescence emission of PbS nanoparticles appears at the red end (700–800 nm) of visible region.[4]

In the present investigation, the TEM analysis showed that the minimum average sizes of PbS nanoparticles were 3 nm. Therefore, a single molecule of G4 PAMAM dendrimer with the hydrodynamic diameter (ca. 4.5 nm) could not stabilize enough the surface of the single inorganic particle with diameter larger than 3 nm,[5] and several dendrimers were necessary to surround the surface of the PbS nanoparticles. On the other hand, as the G4 PAMAM dendrimer molecules are soft and deformable, the dendritic macromolecules within the layer passivating nanoparticles may be highly compressed and flattened on the surface.[5] The reported average thickness of G4 PAMAM dendrimers adsorbed onto inorganic surface was only 0.5–1.8 nm,[5–7] which is much smaller than the diameter of spherical G4 PAMAM dendrimer in water. These results mean that dendrimer are tight-packed on the surface of nanoparticles. It is reasonable that the dense packing would increase the structural rigidity of PAMAM dendrimer and change the microenvironment of the dendrimer, which maybe contribute to form fluorescence centers.[3]

At the present time, the mechanism of this anomalous fluorescence emission is under consideration. However, the 485-nm-emission band was found to have a close relation with the flocculation morphology of PbS/PAMAM nanocomposite. This morphology appeared at an intermediate stage, where well-dispersed PbS nanoparticles were getting very close to each other but did not coalesce into bigger ones. Taken together, the 485-nm emission is likely to be the outcome of flattening or compactness of PAMAM dendrimer on the PbS nanoparticles. On the other hand, the intensity of the 405-nm-emission band took a long time to reach its maximum value, as seen in Figure 2. On the basis of this result, it can be proposed that the longstanding aggregation took place after the formation of PbS/PAMAM dendrimer nanocomposite. In addition, the oxidation of PAMAM dendrimer by oxygen in air maybe also plays a role in the formation of fluorescence moieties, and relevant works are still under investigation.

In summary, the anomalous and strong fluorescence from G4 PAMAM dendrimer was observed on PbS/PAMAM dendrimer nanocomposite; the fluorescence emission significantly depended on the morphology of nanocomposite assembly. The present investigation provides a way to induce strong fluorescence from PAMAM dendrimer and an example to study the interaction between nanoparticles and their surface-bound reagents.

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