Polystyrene nanoparticles stabilize a europium complex

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An improved synthetic method allows the hydrophobic shell of polystyrene nanoparticles to protect a luminescent rare earth complex.

In recent decades, lanthanide-based luminescent nanoparticles have attracted increasingly greater interest as potential high-performance biological probes for immunoassays and cellular imaging. However, most of these complexes are readily destroyed by interaction with other molecules, such as organic or amino acids and multivalent metal ions, during application. Moreover, most of them are insoluble in water, which makes them incompatible with the biological setting in which they are meant to operate. One efficient strategy for overcoming these disadvantages is to embed lanthanide complexes in polymeric nanoparticles that protect the complexes from quenching (i.e., fluorescence-reducing) agents present in the assay medium or in bodily fluid through a hydrophobic (dewetting) mechanism. Such complexes have been reported to have unique luminescent properties.

To the best of our knowledge, the techniques reported are complicated, not generally applicable, or unsuited to scaleup. In contrast, the so-called solvent swelling method represents a universal approach to embedding functional molecules into polymers as no chemical reaction occurs during this physical procedure. Accordingly, we decided to synthesize a europium (Eu) complex—specifically, Eu(TTA)₃Phen, where TTA is thenoyltrifluoroacetone and Phen is 1,10-phenanthroline—embedded in polymer nanoparticles using such a method. Swelling polystyrene (PS) in an acetone solution containing the Eu complex makes it possible to encapsulate the molecules into PS nanoparticles (see Figure 1). We found the as-synthesized composite to be water-dispersible, strongly red-luminescent, and ultra-stable in both strong acids and bases. We further modified the surface of the nanoparticles with chitosan and used them successfully to image cells in vitro.

Transmission electron microscopy showed that the composite nanoparticles had a relatively narrow size distribution with an average diameter of 30–50nm: see Figure 2(A). In addition, photoluminescence spectra showed two broad excitation peaks at 270 and 345nm, and a typical bright line-like emission peak of Eu(III) at 615nm: see Figure 2(B). The as-synthesized PS latex is expected to have a negative zeta-potential (electrokinetic potential of colloidal particles) because of the carboxyl groups of the latex. Indeed, the zeta-potential of the latex measured –48.5mV, but was found to be positive (53.6mV) after absorption of the polycation chitosan: see Figure 2(C). However, the mean hydrodynamic diameter of the latex increased during the post-procedure of washing, embedding, and surface adsorption, a problem that we will address in future work. The lifetime decay constant of Eu complex is 0.619ms in acetone, and it decreased by 36.8% to 0.391ms when the solution was diluted to half the original concentration with water. However, in the case of PS nanoparticles, the lifetime increased by 42.6% to 0.883ms: see Figure 2(D). This finding suggests that water acts as an efficient quencher, hindering its practical application in time-resolved luminescence imaging and immunoassay. In the case of the as-synthesized Eu complex/PS nanoparticles, the complex can be protected from water and other quenchers by the hydrophobic PS shell, which favors its further biological application.

One of the challenges of this work is ensuring the stability of the luminescent nanoparticles in different media. Although much work has gone into overcoming this problem, it is still difficult to obtain stable luminescence signals under lower or higher pH conditions. We...
have shown that the luminescence of our Eu complex can be quenched when pH < 5 or > 10, in sodium dodecyl sulfate solution, or even in phosphate buffer solution (pH = 6.88). We found that the strong red emission of the as-synthesized composite nanoparticles could survive even in 1M hydrogen chloride or 1M sodium hydroxide solution after more than two days (see Figure 3).

In summary, the solvent-swelling method described here uses common materials, such as polymer nanoparticles, that are very easy to synthesize or purchase from commercial sources. The technique requires no expensive devices or complicated procedures. Consequently, many other functional molecules aside from the Eu complex could be embedded into polymer nanoparticles using the solvent-swelling method to achieve better properties. This method is easy to scale up and has great potential in a variety of fields. In future work, we will use the as-synthesized nanoparticles as luminescent labels to design trackable drug carriers, hoping to direct them to an exact target to release drugs embedded within through surface modification.

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References