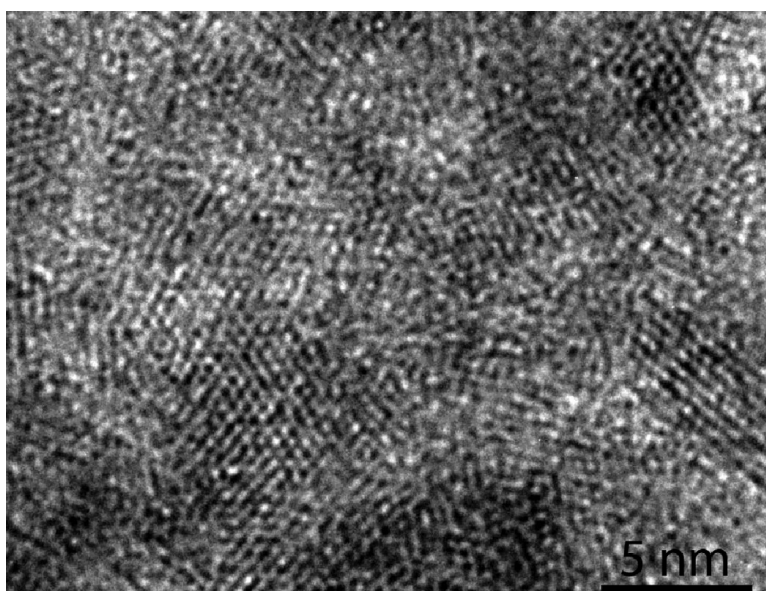


Omni-Composites: A New Strategy for Forming Bulk Nanostructured Materials

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Omni-Composites: A New Strategy for Forming Bulk Nanostructured Materials

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The unique optical properties of nanoparticles and nanocomposites have received considerable attention.^{1–4} Of particular interest are rare earth doped nanocrystals since the lanthanide emissions can be narrow line and possess near unity quantum efficiency. However, nanoparticles can suffer from agglomeration at high loading levels, which results in the undesirable scattering of light. With all of these materials, the quality of the dispersion of the nanomaterials into host materials is not a trivial concern. It is highly desirable to maximize the loading levels of nanomaterials in a host while minimizing scattering.

Colloidal and dispersion stability is often defined by the Hamaker constant, which measures point by point interactions between two separate bodies as a function of their separation.^{5,6} Matching, or at least minimizing, the difference between the Hamaker constant of a nanoparticle with respect to the host material forming the nanocomposite coincides with the matching of refractive indices or, more precisely, dielectric permittivities. This is additionally beneficial for optical applications of nanocomposites since this also minimizes scattering.⁷ This requirement puts additional constraints on the materials selection which must also take into consideration the mechanical, chemical, and optical properties of the matrix.

Alternatively one can modify the surface of the nanoparticle to make it “soluble” or dispersible in a solvent in which the host matrix is mutually soluble. This has been a very popular strategy with optical nanoparticles, and the results have been very promising.⁸ However, when loading levels of nanoparticles exceed 50%, other issues begin to arise. For example, at high nanoparticle concentrations, the amount of ligand solubilizing the nanoparticle into the host can become comparable to the host content and the properties of the host may no longer dominate. This can have detrimental effects to the physical and manufacturing properties of the nanocomposite even if the particles are well-dispersed.

An alternative strategy is to abandon the guest/host composite ideology and shift to the development of nanoparticles that have the exact same composition as the bulk. Many nanoparticles are actually themselves nanocomposite materials. Organic ligands are regularly attached to inorganic and metal particles to create nanoparticles that are dispersible in specific solvents. Despite the fact that it may comprise greater than 50% of the mass of a nanoparticle, the potential of ligands as a structural component tends to be ignored and its use is relegated as a dispersion aid.

In this work, it is proposed that organic ligands can function as the host material itself in a nanocomposite. By developing

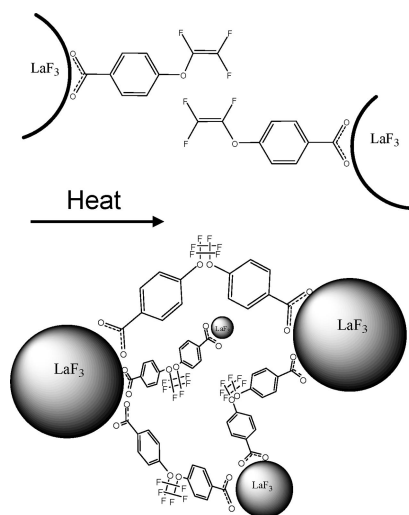


Figure 1. The cyclodimerization of the TFVE ligands forms a bulk cross-linked material.

nanoparticles that have functional ligands, a pressed or gelled nanopowder can be cross-linked into a bulk material without the use of a matrix. In order to distinguish these new types of composites from traditional nanocomposites, they are referred to here as omni-composites because the material is composed entirely (Lat. *omnino*) of composite nanoparticles.

The benefits can be seen in the increased loading levels and decreased scattering. Because a single particle will have thousands of functional ligands, the nanoparticles act as a cross-linker. Because these nanoparticles form highly cross-linked materials (100%), they also should be thermally and chemically stable. Through the use of blends of functional and passive ligands, the percent cross-linking can be controlled.

In this work, LaF_3 nanoparticles with trifluorovinyl ether (TFVE) ligands are synthesized. LaF_3 is an excellent host for rare earth ion dopants due to its low phonon energy and high rare earth solubility. This enables a wide range of emission wavelengths for this host at high efficiency. TFVE acid is a precursor to the perfluorocyclobutyl polymer which has been shown to be an excellent optical polymer.⁹ The carboxyl group acts as the headgroup when deprotonated, and the TFVE terminal group cyclodimerizes with other TFVE acid ligands or TFVE monomer to form a perfluorocyclobutyl ring, as shown in Figure 1.

In order to synthesize nanoparticles with functional ligands, 0.9 mmol TFVE acid and 3.0 mmol NaF were dissolved in 35 mL of H_2O at 75 °C. The pH of the solution was adjusted to 10.6 with NaOH.

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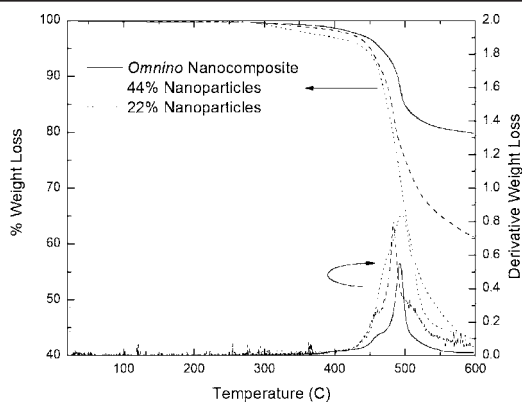


Figure 2. The TGA of LaF₃/6F-PCFB nanocomposites

A total of 1.33 mmol of La(NO₃)₃ and Eu(NO₃)₃ was added dropwise. The solution was stirred for 2 h and cleaned twice in H₂O and ethanol followed by dispersion in dichloromethane and precipitated with ethanol. The particles were allowed to dry for 2 days in a desiccator over P₂O₅. The synthesized particles were easily dispersed in THF when sonicated.

Nanoparticles with diameter between 5 and 10 nm were formed as determined by TEM. A significant shift (1678 to 1548 cm⁻¹) in the peak associated with the vibrations of the TFVE acid's carboxyl group was observed with FTIR. This shift is indicative of the La³⁺ atoms binding to the carboxyl and reducing the vibrational energy.¹⁰

Four different loading levels of the nanoparticles in hexafluoroisopropylidene (6F) derivative PFCB monomer (100, 44, 22, and 0% nanoparticles) were prepared, where the 100% loading levels of nanoparticle is an omni-composite. Polymerization was carried out by heating for 16 h at 150 °C under argon. The temperature was then increased to 180 °C for another 16 h and then cooled over 3 h to room temperature.

The degree of cross-linking was investigated by measuring the solubility and swelling of the nanocomposites. Only the pure 6F-PFCB polymer was soluble in solvent (THF and DCM), and only the 22% nanoparticle composite swelled. After 20 min in THF, the 22% composite had gained 66% of its initial weight (9.5 to 15.8 mg), and after 5 h, it had gained 100% of its initial weight. The 44% nanoparticle composite and the omni-composite were not soluble in either solvent and did not exhibit any detectable swelling over a period of days.

Thermogravimetric analysis (TGA) was performed to determine what percent of the nanoparticles was ligand and also to determine the onset of thermal degradation (Figure 2.). The omni-composite, traditional nanocomposites, and pure 6F-PFCB polymer all had similar thermal stability with the onset of degradation occurring at approximately 300 °C and the degradation rapidly accelerating at 450 °C. It was also determined from TGA that the pure nanoparticles were composed of 22 wt % ligand. This indicates that the omni-composite reached a loading level of 78% optically active material (Eu³⁺-doped LaF₃).

The nanocomposites were optically transparent, and the transmission spectra (Figure 3a) show that the omni-composite has significantly lower absorptions in the UV. This is expected due to the high concentration of LaF₃ in the composite. This

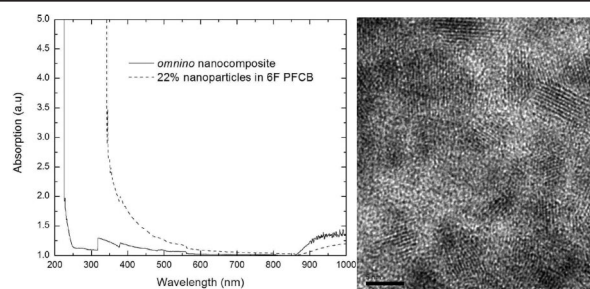


Figure 3. (a) A large shift in the electronic absorption edge is seen in the transmission spectra of the omni-composite. (b) A high-resolution TEM image of the omni-composite shows the density of particles.

shift is predicted by using a weighted average of the materials composition and the electron absorption tail.

The increased loading levels can be seen spatially in the high-resolution TEM imaging of the cross sections of the omni-composite in Figure 3b.

For rare earth doped materials, we expect to see the emission intensities increase proportionately to the increase in the loading levels of the nanoparticle since there are no concentration quenching effects as are common with quantum dots (concentration quenching is an issue with the doping level of rare earth ions within a nanoparticle, however). In this way, the intensities of the omni-composite are ~8 times higher than those of a traditional nanocomposite where loading levels of 10% nanoparticles in polymer have been achieved.

In conclusion, a new method for creating optical materials from nanomaterials has been developed which uses the cross-linking of ligands to provide bulk materials with loading levels of nanoparticles approaching 80 wt %. The method of forming the omni-composite allows for bulk materials to be formed without a host matrix in the traditional sense. The result is a processable nanocomposite with the optical properties close to that of an inorganic material.

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