

Polymer and Colloid Highlights

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Optical Upconversion in Polymeric Nanoparticles

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Luminescent materials that emit light of a higher wavelength than that used for excitation (Stokes process) are ubiquitous and present in everyday-life applications that range from highlighting pens to biological assays to optical brightening agents. However, for many applications, such as *in vivo* imaging, solar harvesting, or drug delivery, an inverse (anti-Stokes) process would be useful, in which the energy of several photons is combined to produce a radiation of higher energy. This phenomenon is known as *light upconversion*. While several processes are known to allow this optical process, few bear as much promise for practical applications as low-power sensitized upconversion based on triplet–triplet annihilation (TTA-UC). The main advantage of this process, which involves a series of consecutive photophysical events including absorption by a sensitizer, intersystem crossing to a triplet state, triplet–triplet energy transfer to an emitter, triplet–triplet annihilation of two emitter species, and finally emitter fluorescence, emanates from the fact that it is feasible at low-power densities and with non-coherent light. While TTA-UC has long been known to occur in solutions of appropriate sensitizer/emitter pairs, it has taken almost 50 years to realize this process in solid materials.^[1]

A breakthrough was made when it was shown that rubbery polyurethane and poly(ethylene oxide-*co*-epichlorohydrin) were excellent hosts for TTA-UC sensitizer/emitter pairs, as the chromophores are somewhat mobile and the bimolecular processes happen quite efficiently.^[2,3] Capitalizing on these findings, we extended this method to develop upconverting polymeric particles.^[4] Thus, *n*-butylacrylate was polymerized in the presence of divinylbenzene in a surfactant-free emulsion polymerization to afford rubbery, cross-linked nanoparticles with an average diameter of 320 nm. These particles were subsequently doped with a mixture of palladium octaethylporphyrin (PdOEP) and 9,10-diphenylanthracene (DPA). Transmission electron micrographs and dynamic light scattering revealed that the particles disperse well in water (Fig. 1). Characteristic upconverted blue fluorescence with a peak wavelength of 440 nm was observed when non-deaerated aqueous suspensions of the particles were excited at 532 nm, even at a power density of as low as 0.04 W cm⁻². The possibility to realize TTA-UC under such conditions appears to be an important stepping stone towards their use in biomedical settings. Moreover, we demonstrated that it is readily possible to convert such lattices into upconverting films, which suggests that the design approach may permit the processing of upconverting polymers as coatings or paints.

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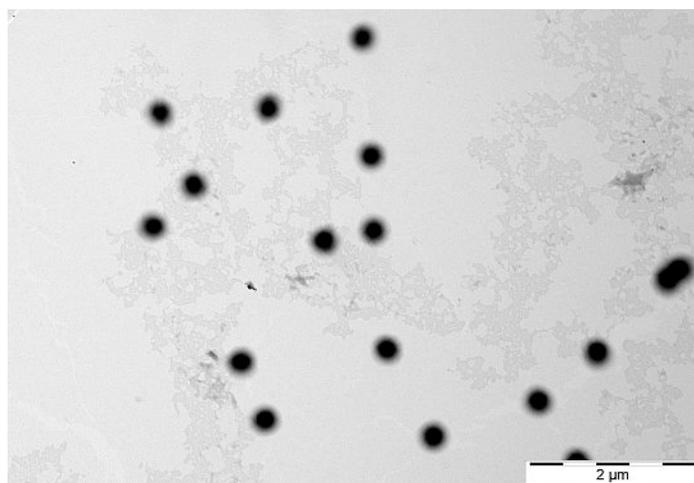
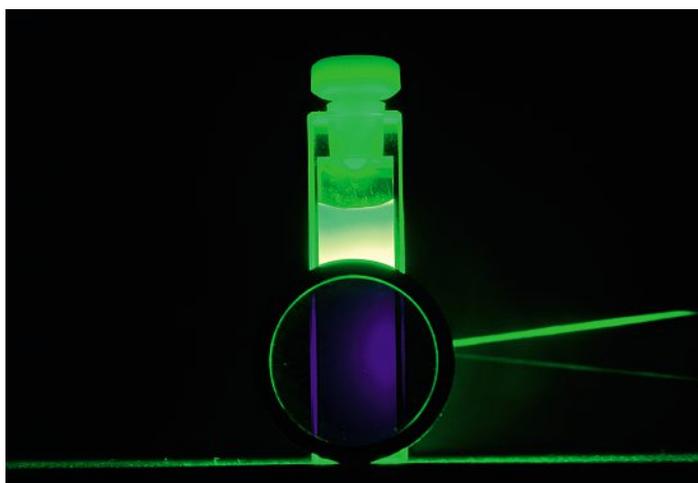


Fig. 1. (Left) Upconverted blue light from a green 543 nm HeNe laser by a colloidal suspension of dye-doped (DPA/PdOEP) cross-linked poly(*n*-butyl acrylate) nanoparticles. The 500 nm short-pass edge filter that covers part of the sample suppresses the scattered green light incident from the laser. (Right) Transmission electron micrograph of the DPA/PdOEP-doped nanoparticles.

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