Low-Power Upconversion in Dye-Doped Polymer Nanoparticles

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Examples of nanoscale low-power upconverting systems are rapidly increasing because of their potential application in numerous areas such as bioimaging or drug delivery. The fabrication of dye-doped cross-linked rubbery nanoparticles that exhibit upconversion even at relatively low power densities is reported here. The nanoparticles were prepared by surfactant-free emulsion polymerization of n-butylacrylate with divinylbenzene as a cross-linker, followed by dyeing of the resulting particles with a two-chromophore system composed of a palladium porphyrin sensitizer, and diphenylanthracene. Blue emission (≈440 nm) of these systems was observed upon excitation at 532 nm. In addition to their optical properties, the particles were characterized by electron microscopy and dynamic light scattering.

1. Introduction

Optical upconversion (UC), that is, the conversion of light into radiation of a shorter wavelength, is useful for a plethora of applications, for example, solar harvesting, bioimaging, drug delivery, and optical data storage.[1–3] Examples of optical UC schemes include second and third harmonic generation, energy transfer UC (e.g., in lanthanides), and excitation via two-photon absorption.[4] All of these rather well-established pathways require coherent, high-intensity excitation by (pulsed) high-power lasers.[1] They can therefore not readily be exploited in the aforementioned applications, in which the ability to upconvert

low-power, noncoherent, continuous-wave excitation is either desirable or a must. About 50 years ago, Parker and Hatchard[5] showed that low-power UC can be achieved by way of triplet–triplet annihilation (TTA-UC) in multichromophore systems comprising a triplet sensitizer and an emitter. The generally accepted mechanism for liquid solutions of these chromophores is that light is absorbed by the triplet sensitizer, whose first singlet excited state is converted into a triplet upon intersystem crossing. Energy transfer to an emitter and triplet–triplet annihilation eventually causes singlet fluorescence by the emitter (Figure 1). Interestingly, for almost half a decade, TTA-UC had been confined to liquid solutions of sensitizer–emitter pairs. Recently, it was shown that this effect can be achieved in polymeric materials.[6,7] Key to efficient UC in polymer systems was the use of rubbery matrix polymers that allowed for facile diffusion of excited states, thereby supporting the bimolecular photophysical steps required for photon UC. Building upon this work, we here report low-power upconverting nanoparticles (UCNPs) based on a similar design approach. UCNPs are receiving a great deal of attention in the context of medical applications such as imaging and controlled drug release.[2,8,9] Lanthanide-doped nanocrystals such as $NaYF_4$ doped with Er^{3+} or Yb^{3+} represent the current state of the art,[8–11] but they require significant

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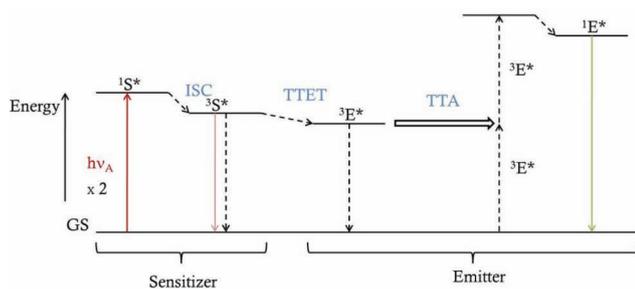
Figure 1. Simplified energy level diagram of the triplet–triplet annihilation process in the studied upconverting nanoparticles. Solid and dashed lines represent radiative and nonradiative processes, respectively. Upon light absorption, the first singlet excited state ($^1S^*$) of the sensitizer is populated. Intersystem crossing (ISC) to the sensitizer's first triplet excited state ($^3S^*$) and triplet–triplet energy transfer (TTET) populate the emitter's first triplet excited state ($^3E^*$). Triplet–triplet annihilation (TTA) leads to population of the emitter's first singled excited state ($^1E^*$), which relaxes to the ground state, causing delayed fluorescence.

amounts of rare earth ions and the power density necessary for excitation of these materials is still relatively high. The possibility to exploit a TTA effect for the design of UCNPs was demonstrated by Zhang and co-workers,[12] who reported TTA-UCPNs that were made by deposition of perylene onto Ir nanoparticles. They further extended this work to make nanowire waveguides with white light outcoupling.[13] Wohnhaas and co-workers[14] utilized a microemulsion process to incorporate upconverting pairs into polymeric microcapsules for biological imaging in cells. Most recently, Monguzzi et al.[15] reported UC from dual-dye-loaded polystyrene nanoparticles with an average diameter of below 20 nm. These particles, produced by a microemulsion polymerization process, show UC at low-power densities, which is, in view of their glassy nature, very surprising. This observation appears to be related to the very small size and the ensuing confinement, which supports efficient exciton migration within each particle. The present study demonstrates an alternative, elastomer-based design approach to such materials, which permits TTA-UC in particles with diameters in the range of a few hundred nanometers.

2. Experimental Details

2.1. Materials and Sample Preparation

All materials were bought from Sigma–Aldrich and were used as received. In a two-necked round-bottom flask equipped with a condenser, *n*-butyl acrylate (nBA, 20 mL) and deionized water (200 mL) were combined. The mixture was heated while stirring at 300 rpm. In a separate container nBA (29.4 mL) and divinyl benzene (DVB, 0.6 mL, Aldrich, Lot # 06212JH-437) were combined and then added to the stirred nBA/water emulsion. After stirring the mixture for about 10 min at reflux, potassium

persulfate (KPS, 0.2 g) was added at once. The reaction mixture was put under nitrogen and stirred under reflux for 2 h before it was cooled to room temperature. A fraction of the nanoparticle suspension thus produced was then centrifuged in a 2.5 mL Eppendorf tube, the supernatant was removed and the nanoparticles were resuspended in tetrahydrofuran (THF) to remove the water. The washing procedure was repeated five times. After the last washing cycle, the nanoparticles were infused with a THF solution containing diphenylanthracene (DPA, 1 mg mL^{-1}) and palladium (II) octaethylporphyrin (0.2 mg mL^{-1}) and left to stand for 12 h. The dispersion was then centrifuged and the supernatant was removed. The tube was then cooled to 0 °C, which helped to prevent aggregation, EtOH (0.1 mL) was added and water (1.5 mL) was subsequently added. The dispersion was then washed three times with water by centrifugation and the particles were used as produced [0.1 wt% DPA and 0.05 wt% Pd(II) octaethylporphyrin (PdOEP)]. Undyed particles were isolated by applying the same method, but neat THF (without dye) was used for the 12 h infusion step. Likewise, nanoparticles dyed with DPA only or PdOEP only were produced by using saturated THF solutions of only DPA or only PdOEP during that 12 h infusion step to produce particles with the same concentrations.

2.2. Transmission Electron Microscopy

For the study of the size and morphology of the synthesized particles, transmission electron microscope (TEM) images were obtained from a TEM (TEM-CM100, Philips) at 80 keV. A typical sample preparation for TEM experiment is as follows. The particle dispersion was concentrated using a laboratory centrifuge at 10 000 rpm followed by drying one droplet containing nanoparticles at a concentration of ≈1 wt% onto a 300 mesh carbon-coated grid.

2.3. Dynamic Light Scattering

Dynamic light scattering (DLS) measurements were performed on an LS instrument (Switzerland) goniometer system equipped with a HeNe-Laser operating at a wavelength of $\lambda_0 = 632.8$ nm. An aqueous suspension of a concentration of 0.01 g L^{-1} was used for this purpose. Average particle hydrodynamic radii were determined from the Einstein –Stokes relation using the diffusion coefficient measured from the slope of the decay rate as a function of the square of the scattering vector. The decay rate was measured at scattering angles varying from 16° to 136° every 15°, at a temperature of 20 °C.

2.4. Emission Experiments

Dilute aqueous suspensions (0.5% w/w nanoparticles in water) of the upconverting polymeric nanoparticles containing DPA and PdOEP and reference nanoparticles containing DPA only, or PdOEP only were excited with a frequency doubled Nd:YVO$_4$ continuous wave laser with an emission centered around 532 nm. The laser beam was lightly focused resulting in a spot area of ≈5 × 10^{-4} cm^2 (measured by checking the variation of intensity with decreasing pin hole sizes). The excitation power was measured with an optical power meter (Newport 1830-C with detector
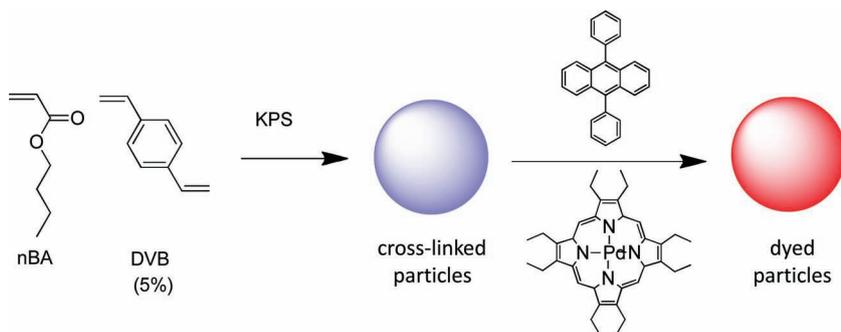
Scheme 1. Illustration of the preparation of the upconverting nanoparticles by surfactant-free polymerization of n -butylacrylate (nBA), divinylbenzene (DVB) with potassium persulfate (KPS) as a radical initiator followed by a dying procedure in tetrahydrofuran.

head 818-UV) and varied with neutral density filters in the range 0.02–2.3 mW, corresponding to an average power density of 0.04–4.6 W cm⁻². The emission from the nanoparticle dispersion was collected with a lens, sent through a high-pass filter with a band edge at 500 nm to suppress scattered excitation light, and spectrally dispersed in spectrometer (Acton Research SpectraPro 2300i with a 150 grooves/mm grating). Spectra were recorded with a cooled CCD camera (Princeton Instruments PIXIS 100). Direct fluorescence measurement was performed by exciting DPA at 406 nm with a pulsed diode laser with a repetition rate of 20 MHz and a pulse duration of ≈60 ps.

3. Results and Discussion

A surfactant-free emulsion polymerization process was employed to create polymeric host nanoparticles.[16] One advantage of this technique is that the size and composition of the particles can be tailored at will to form numerous types of complex architectures.[17,18] Based on the earlier finding that a rubbery matrix with low glass transition temperature (T_g) is the key to efficient low-power UC in solid polymeric materials,[7] nBA was polymerized in water with 5 wt% of divinylbenzene as a cross-linker and potassium persulfate (KPS) as initiator (Scheme 1). Surfactant-free emulsion polymerization (SFEP) proceeds by a traditional emulsion polymerization as described by Harkins,[19] except that no additional surfactant is added to stabilize the emulsion. Instead, the latex particles are self-stabilized by the charges present on chemically bound groups (e.g., persulfate from the KPS initiator) to prevent flocculation, and are generally believed to form via homogeneous nucleation. The T_g of the nBA nanoparticles thus produced was determined by differential scanning calorimetry to be −42 °C (Figure S1, Supporting Information). Unlike in the recent nanoparticles reported by Monguzzi et al.,[15] where confinement was used to address the problem of excited-state migration in a glassy matrix, the system reported here permits synthesis of larger particles as excited-state

migration is facilitated by the increased (rotational) mobility of the chromophores above the T_g of the host polymer.[7]

Adapting a known process to incorporate organic and inorganic components into microgels,[16,20] the nBA nanoparticles were placed into a THF solution saturated with a well-known TTA-UC sensitizer/emitter pair, PdOEP (≈0.2 mg mL⁻¹) and 9,10-diphenylanthracene (DPA, ≈1 mg mL⁻¹), and were allowed to swell with the solvent/dye mixture. The hydrophobic nature of the dyes necessitated the use of organic solvent to swell the lyophilic nBA cross-linked particles similarly to the work of Lange.[20] The nBA nanoparticles were subsequently separated from the dye solution, resuspended in water, and washed thoroughly with water to remove the organic solvent. The dyed nBA nanoparticles were found to contain ≈0.1 wt% of DPA and 0.05 wt% of PdOEP. The particle size and size distribution were determined using TEM and light scattering. TEM images showed that the dyed nBA nanoparticles were spherical in nature with an average diameter of ≈322 nm (Figure 2). The particles containing the dye mixture exhibited great mass contrast due to the presence of PdOEP. The micrographs showed that the nanoparticles were monodisperse and mostly well individualized. DLS measurements of unfiltered solutions, performed at angles ranging from 16° to 135° every 15°, resulted in an average hydrodynamic radius of ≈178 ± 23 nm (Figure S4, Supporting Information), confirmed the TEM data and
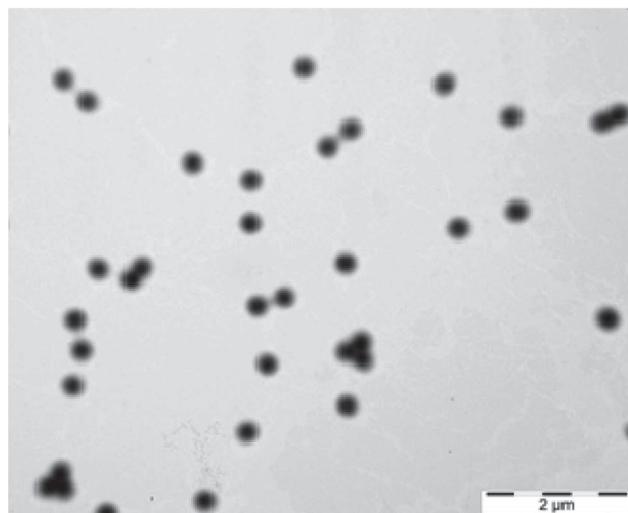
Figure 2. Transmission electron micrograph of the upconverting nanoparticles studied. These DVB cross-linked nBA nanoparticles contain ≈0.05 wt% of PdOEP and ≈0.1 wt% of DPA and were imaged without further staining.

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indicated that the dimers and trimers observed in the micrograph were due to drying (Figure S6, Supporting Information).

The UC effect of the new nanoparticles was probed by exciting colloidal aqueous suspensions with a continuous wave laser source at 532 nm using a short pass 500 nm edge filter on the detection side and a set of neutral density filters on the excitation side to vary the incident power densities between 0.04 and 4.6 W cm^{-2}. The wavelength was chosen to selectively excite the PdOEP Q-band at 543 nm and avoid excitation of DPA, which has a main absorption band at 372 nm. Gratifyingly, aqueous suspensions of nanoparticles comprising both DPA and PdOEP displayed upconverted fluorescence (Figure 3). The emission spectra match the fluorescence spectrum of

Figure 4. Upconversion of a dried sample of dyed nBA nanoparticles excited at 543 nm through a 500 nm short pass filter.

a)

b)
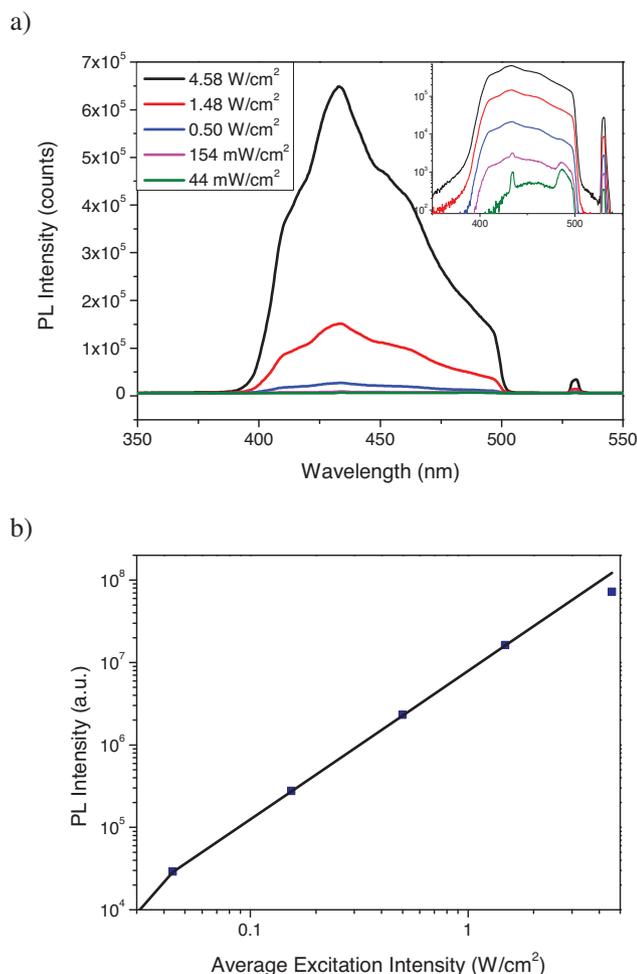
Figure 3. (a) Upconverted emission spectra of colloidal aqueous suspensions (0.5% w/w nanoparticles in water) of the upconverting nBA nanoparticles containing ≈0.05 wt% of PdOEP and ≈0.1 wt% of DPA as a function of incident power (inset: plotted in logarithmic scale). (b) Spectrally integrated emission intensity extracted from the spectra shown in (a) versus excitation power density. The data (excluding the highest value) was fitted with a power law, yielding an exponent of 1.8.

DPA well (as observed for suspensions of reference particles comprising only DPA that were excited at 406 nm; see Figure S2, Supporting Information) (Figure 3a). Note that the spectra are cut off above ≈500 nm due to the use of a short-pass edge filter and that some residual excitation is observable around 532 nm. One advantage of this method resides in the possibility to cast films from the dyed nBA nanoparticle dispersions that also perform UC (Figure 4), which paves the way for utilization in coatings and paints. The fact that UC sets in only at excitation power densities that are one order of magnitude higher than the previously reported films is attributed to the low concentration of DPA inside the particles (≈0.1 wt%) compared to the bulk material (≈1 wt%; see Figure S5, Supporting Information). Current investigation to tether the dye pair to a polymerizable handle will help circumvent that issue.

Reference experiments with aqueous colloidal suspensions of particles comprising only DPA or only PdOEP or a mixture of both these particle types did not show any appreciable emission when excited under identical conditions as the DPA–PdOEP-dyed nanoparticles (Figure S3, Supporting Information). These results further confirm the proposed mechanism and support the notion that the energy transfer occurs indeed within the particles and not in solution because triplet energy exchanges are usually governed by Dexter-type transfer,[21] which requires interactions on a sub-nanometer length scale.

The dependence of the sensitized UC emission intensity of the upconverting nanoparticles on the incident power density is provided in Figure 3b. A linear regression of the data with a power law function results an exponent of 1.8 and reveals the nonlinearity of the UC process and supports that this effect is indeed a bimolecular process, as expected for the proposed underlying mechanism. The point of highest intensity deviates from the approximately quadratic dependence and tends toward a more linear behavior.

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501

This finding corroborates previous reports of a breakdown of the quadratic input–output intensity relationship above a certain incident power threshold.[22,23] While the particles as such cannot be utilized for biomedical applications due to their large size and their composition, one can easily envision how straightforward alterations (e.g., shorter polymerization times, other chromophore systems, copolymerization with oligoethylene glycol methacrylate, etc.) could help make them suitable probes for bioapplications.[24]

4. Conclusions

In conclusion, it was shown that the noncovalent integration of a judiciously chosen triplet sensitizer–emitter pair into a slightly cross-linked, rubbery host polymer allows one to create upconverting polymer nanoparticles, which show delayed fluorescence at incident power densities as low as 0.04 W cm^{-2} and display the nonlinear relationship between incident light intensity and UC emission intensity that is expected for the proposed mechanism. The possibility to disperse these nanoparticles in water and observe UC without deaeration makes the new materials highly attractive upconverting media.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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