

Effect of Particle Size and Capping on Photoluminescence Quantum Efficiency of 1,3,5-Triphenyl-2-pyrazoline Nanocrystals

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Organic nanocrystals of 1,3,5-triphenyl-2-pyrazoline (TPP) with a series of sizes were synthesized by reprecipitation method. The luminescence quantum efficiency of TPP nanocrystals increases from 24.2% for the nanocrystals with an average size of 300 nm to 34.6% for those with an average size of 20 nm. Surface capping by polyvinyl pyrrolidone (PVP) will improve the quantum efficiency of TPP nanocrystals. The size-dependence and capping-induced variation of the luminescence quantum efficiency was elucidated in viewpoint of aggregation quenching and the equilibrium between the TPP monomers and the aggregates in TPP nanocrystals.

Keywords organic nanocrystals, reprecipitation method, quantum efficiency, capping effect

Introduction

Nanometer-scale materials promise to be of fundamental and technological importance in the development of next-generation electronic and optoelectronic devices. Nanocrystals of inorganics have been one of the most actively pursued fields of science due to their unique optical and electrical properties. The electronic states of inorganic nanoparticles and their evolution as a function of size have been well documented by numerous spectroscopic studies over the last decade.¹⁻⁸ However, a paucity of work on the nanoparticles prepared via small organic molecules reveals that this research area is only in its infancy so far.^{9,10} Organic materials, whose properties are based on their component molecules, are much more versatile than the inorganic ones, whose properties derive from their component atoms. In addition, the properties of organic molecules, whether optical or electrical, can be controlled conveniently by conventional organic synthesis. Nakanish and co-workers⁹ reported the synthesis of perylene and polydiacetylene nanoparticles and found that the nanoparticles of polydiacetylene were a kind of promising material for third-order nonlinear optics. Our group also reported the size-dependent optical properties¹⁰ exhibited by nanoparticles of a pyrazoline derivative, PDDP. Pyrazolines have been widely employed in the construction of optoelectronic devices such as

organic light-emitting diodes (OLEDs) and flat panel display. For organic emissive materials used in OLEDs, aggregation quenching is one of the barriers to high quantum efficiency. Achieving luminescence efficiency is still a challenge that scientists have been facing. Photoluminescence quantum efficiency is critical in successful design of the systems because the quantum efficiency of electroluminescence depends on that of the photoluminescence [The OLED electroluminescent efficiency (η_{EL}) is related to the photoluminescent efficiency (η_{PL}) of the materials by means of the following equation: $\eta_{EL} = \eta_{PL} \eta_E \eta_T \chi$, where η_E is the light-escape efficiency, η_T the energy-transfer efficiency, and χ the fraction of electrons participating in luminescence].

In this paper, a fluorescent organic molecule, 1,3,5-triphenyl-2-pyrazoline (TPP) was used as a model compound to synthesize the organic nanocrystals through reprecipitation method.^{9,10} The different-size TPP nanocrystals were obtained by controlling the aging time, that is to say, taking samples for measurement from their aqueous dispersion at different time intervals. The evolution of the photoluminescence quantum efficiency of TPP nanocrystals was investigated as a function of average particle size. The change in quantum efficiency of the TPP nanocrystals was explained in viewpoints of the aggregation effect and the surface capping effect.

Experimental

The model compound, 1,3,5-triphenyl-2-pyrazoline (TPP), was synthesized according to reported method^{11,12} and purified by liquid chromatography. NMR and MS were used to confirm its structure, which is shown as the inset of Fig. 1. Polyvinyl pyrrolidone (PVP, average M.W. 3500) and quinine sulfate were purchased from ACROS and used as received. Ultrapure water (18.2 M Ω ·cm) produced from Millipore-Q Gradient apparatus was used in all experiments.

The organic nanocrystals of TPP were synthesized by reprecipitation method. TPP was insoluble in water but soluble in some organic solvents such as acetone and ethanol. In a

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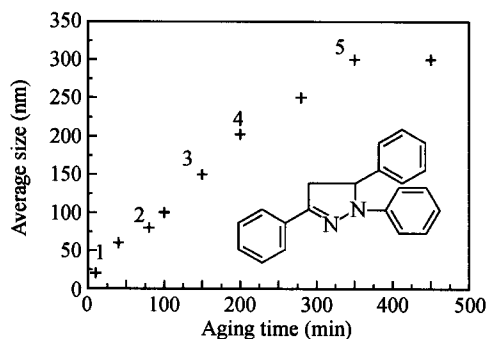


Fig. 1 Average sizes of TPP nanocrystals determined by DLS technique versus aging time. The inset is the molecular structure of 1,3,5-triphenyl-2-pyrazoline.

typical synthesis, 30 μL of TPP stock solution (1.10×10^{-3} mol/L in ethanol) was quickly injected into ultrapure water with stirring at 20 $^{\circ}\text{C}$. The TPP molecules began to conglomerate and the nanocrystal suspension was obtained. Average size of TPP nanocrystals dispersed in water was tuned by variation of the aging time and evaluated by the dynamic light-scattering (DLS) technique using Zetaplus BI-9000 (Brookhaven Instrument Corporation). For example, TPP nanocrystals with the average size of 80, 200 and 300 nm were obtained when samples were taken out at the aging time of 65, 200 and 350 min, respectively. PVP solution was added into the nanocrystals solutions at different aging time. The size and shape of the nanocrystals were observed through a JSM-6301F (JEOL, Japan) field emission scanning electron microscope (FESEM) operated at 5 kV. The measurement of XRD for TPP nanocrystals was carried out on D/max-2400 (RINT-2400) X-Ray diffractometer with an X-ray source of Cu K α at 40 kV and 120 mA. UV-Vis absorption spectra were recorded on Shimadzu UV-1601PC spectrophotometer. The aqueous dispersion of TPP nanocrystals was placed in 1-cm quartz cuvette and their absorption and corresponding photoluminescence spectra were acquired. The samples were purged for 20 min to remove oxygen from solution with nitrogen before the optical characterization. Photoluminescence spectra were measured with a Hitachi F-4500 fluorescence spectrometer. Luminescence quantum efficiencies were deter-

mined by comparing with that of solution of Quinine sulfate in H_2SO_4 (0.05 mol/L), which is known to fluoresce with quantum efficiency of 0.546. All the experiments were carried out at (20 ± 1) $^{\circ}\text{C}$.

Results and discussion

A series of TPP nanocrystals with different sizes was synthesized by changing the aging time. Fig. 1 shows the evolution of average sizes of the nanocrystals as a function of time after injection of TPP solution into ultrapure water, in which the values of the average particle sizes were determined by DLS technique. It is obvious that the size of particles increases with time extending. The average particle size almost keeps at a stable value (300 nm) when the aging time is longer than 350 min. FESEM images of TPP nanocrystals are shown in Fig. 2, the average sizes being 80, 200 and 300 nm, respectively, which are consistent with those by DLS measurements. The existence of diffraction peaks in XRD patterns of the TPP nanoparticles indicates that the as-prepared TPP nanoparticles are crystalline.

UV-Vis absorption spectra [Fig. 3(A)], were recorded at the same time intervals during the growth of TPP nanocrystals in water at 20 $^{\circ}\text{C}$. With the growth of TPP nanocrystals, the absorption band shifts to longer wavelength. Curve fitting results indicate that the band is composed of two peaks. One peak at 360 nm is attributed to the absorption transition of monomer and the other at longer wavelength is due to *J*-aggregate.¹³ Obviously, with increasing the nanocrystal size, the *J*-aggregate band gradually shifts to longer wavelength. The photoluminescence spectra in Fig. 3(B) exhibits a structureless band centered at 450 nm and there is no change in peak position, except for decrease in luminescence intensity with the growth of TPP nanocrystals. The influence of average particle size on the luminescence quantum efficiency of TPP nanocrystals is shown in Fig. 4. It can be seen that the quantum efficiency of the nanocrystals decreases from 34.6% for the particles with an average size of 20 nm to 24.2% for those with an average size of 300 nm. To explain the mechanism of decrease in luminescence quantum efficiency of

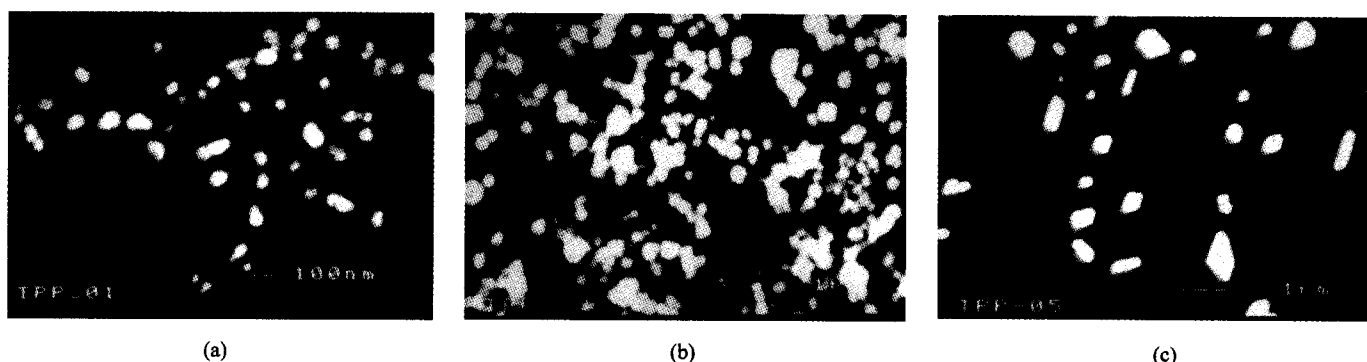


Fig. 2 FESEM images of TPP nanocrystals (a) 80 nm, P.D. = 0.078; (b) 200 nm, P.D. = 0.103; (c) 300 nm, P.D. = 0.137 [Here P.D. is the abbreviation of polydispersity obtained by DLS measurement].

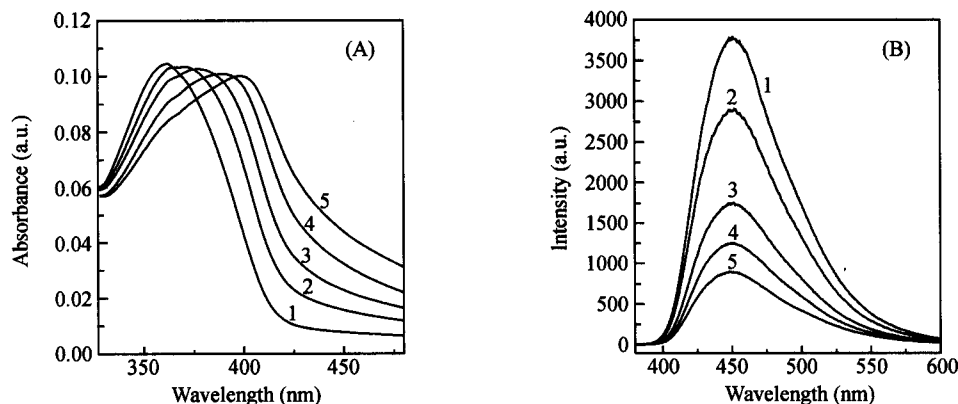


Fig. 3 UV-Vis absorption spectra (A) and photoluminescence spectra (B) of TPP nanocrystals aqueous dispersion measured at some time intervals during particle growth at 20 °C. Number 1 to 5 means that the corresponding sample was taken at the same aging time as that in Fig. 1.

TPP nanocrystals as the particle size increases, it is necessary to know the factors that affect the quantum efficiency of the particles. It is known¹³ that the luminescence quantum efficiency of inorganic nanocrystalline (such as colloidal CdS, ZnS, CdSe, etc.) is dependent on the nature of the surface,¹⁴ the solvent¹⁵ and the surface-to-volume ratio.¹⁵ The above-mentioned factors are, in the final analysis, ascribed to the surface defect sites which are responsible for non-radiative recombination. The probability for non-radiative decay via surface defect sites can be expected to increase as the particle size decreases due to increased surface-to-volume ratio. Then the radiative process decreases because non-radiative recombination occurs through the surface defects. Therefore, the luminescence quantum efficiency of the particles should increase with the increase of particle size. However, the quantum efficiency of TPP nanocrystals decreases with the increase of particle size. This implies that the surface defect sites are not the dominant factor to affect the quantum efficiency of the TPP nanocrystals. The same preparation condition of different-sized TPP nanoparticles also excludes the possibility of the solvent effect on the quantum efficiency.

The size-dependent bathochromic absorption of organic nanoparticles of TPP, as reported in our previous work,¹³ was mainly attributed to the increased ratio of *J*-aggregate with the growth of the particles. Monomer and *J*-aggregate of TPP molecules coexist in TPP nanoparticles and the percentage of *J*-aggregate increases when the particle size increases. When the particle size increased from 60 nm to 300 nm, the area of *J*-aggregate absorption peak increased from 0.3% to 16% and that of the monomer decreased. The quantum efficiency of the fluorescence of the monomer is usually much higher than that of the dimer or higher aggregate.^{17,18} Moreover, the emission from an aggregate depends critically on the geometrical arrangement of molecules within the aggregate.¹⁹ From shift of the peak position in the absorption spectra, it is inferred that the angle²⁰ between the transition dipole and the molecular axis of the aggregate increases with growth of the nanocrystals, lowering the quantum efficiency of emission from the aggregate. Therefore it is proposed that the formation and structural change of the *J*-aggregate is the principal

reason responsible for the decreased luminescence quantum efficiency of TPP nanocrystals with the increase of particle size.

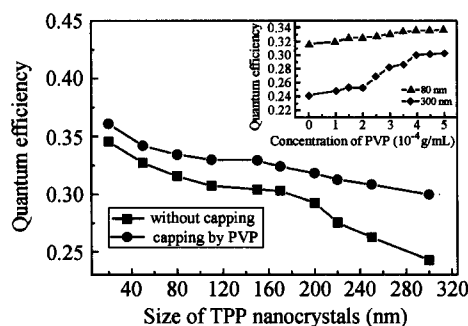


Fig. 4 Influence of average particle size on the photoluminescence quantum efficiency of TPP nanocrystals. Solid square; without capping; Solid circle; with capping by a water-soluble polymer PVP at the concentration of 0.40 mg/mL; Inset: influence of concentration of capping agent PVP on the photoluminescence quantum efficiency of TPP nanocrystals with the sizes of 80 and 300 nm.

It is known that the luminescence quantum efficiency of inorganic nanocrystals can be improved significantly by surface capping. A water soluble polymer, PVP, was used as capping agent to investigate the capping effect on the photoluminescence quantum efficiency of TPP nanocrystals. An increase in quantum efficiency was observed for the TPP nanocrystals with different sizes in the presence of the capping agent (see inset of Fig. 4). It is noted that the quantum efficiency of the nanocrystals with larger size increased more significant than that of smaller ones after surface capping. When the concentration of PVP is 0.40 mg/mL, the quantum efficiency of the 20 nm nanocrystals only increases from 34.6% to 36.1%, while that of the 300 nm nanoparticles increases from 24.2% to 30.0%. As displayed in inset of Fig. 4, the quantum efficiency of TPP nanocrystals with sizes of 80 and 300 nm are improved with increasing the concentration of capping agent. The quantum efficiency reaches a maximum at/beyond a concentration of PVP. This means that the surface capping will lead to an increase in luminescence

quantum efficiency of TPP nanocrystals and the mechanism of the surface capping effect on the luminescence quantum efficiency of the TPP nanoparticles should be different from that of inorganic ones. In our experiment, the nanocrystals are prepared by reprecipitation method, which is based on the different solubility of the organic molecules in two different solvents. The nanocrystals are actually in an equilibrium process-precipitation and dissolving. The molecules at the periphery of the nanocrystals usually escape from the aggregate, forming free monomers. Similar to the function of gelatin in controlled precipitation process,²¹ the adsorption of PVP on TPP nanocrystals is controlled by hydrophobic interaction. The PVP molecules rearrange their conformation, thus making polar head oriented towards the water phase while the non-polar carbon chain domains are closely bounded to the surface of the organic nanocrystals. The hydrophobic microenvironment around the TPP nanocrystal makes it possible for the aggregate on the surface of nanocrystals to dissolve into the carbon chain as monomers. As a result, more and more aggregates on the surface of larger nanocrystals (*e.g.* 300 nm) will be transferred into monomer, leading to more significant increase of quantum efficiency in larger particles than that in smaller ones.

Conclusion

In summary, organic nanocrystals of TPP ranging in average sizes from 20 nm to 300 nm were successfully prepared using the reprecipitation method. Photoluminescence quantum efficiency of the TPP nanocrystals can be tuned readily by changing the particle sizes without increases in complication of the preparation. Surface capping of the organic nanocrystals by PVP can improve their quantum efficiency to some extent because of the existence of equilibrium between the monomers and the aggregates. Aggregation quenching plays a crucial role in decrease of the photoluminescence quantum efficiency of the organic nanocrystals when the particle size increases. The size-tunability of luminescence quantum efficiency is explained in term of aggregation quenching in TPP nanocrystals. It is expected that the luminescence quantum efficiency of organic nanoparticles can be improved by decreasing their size and modifying their surface by capping agents. Such a study will contribute useful information

for using organic nanoparticles as building blocks of electroluminescent devices.

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