Highly bright and sharp light emission of a single nanoparticle of crystalline rubrene†

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We report on the fabrication and nanoscale luminescence characteristics of an isolated rubrene single nanoparticle (NP). A solvent-vapor annealing process changed pristine rubrene NPs, prepared by a reprecipitation method, to perfect crystalline NPs. The formation and structural properties of crystalline and non-crystalline rubrene NPs were studied through SEM, HR-TEM, and X-ray diffraction experiments. The nanoscale photoluminescence (PL) characteristics and the luminescence color of the rubrene single NP were measured using a high-resolution laser confocal microscope with color charge-coupled device images. In comparison with the pristine rubrene NPs, the crystalline NPs exhibited highly bright and sharp light emission. The main PL peak at 561–562 nm for the crystalline rubrene single NP had a relatively narrow line-width and became more dominant through a solvent-vapor annealing. The enhanced and sharp light emission of the crystalline rubrene single NP originated from the strong π–π interaction of rubrene molecules along the major crystalline axis in the nano-sized structure.

Introduction

Inorganic and organic nanoparticles (NPs) afford excellent photonic, electrical, and magnetic properties in addition to biocompatibility, and were developed for both fundamental nanoscale research and application to optoelectronic devices and bio-labelling.1–3 The diameter and crystallinity of NPs control the intrinsic properties, such as the optical absorption and photoluminescence (PL).4,5 For example, Bawendi and Rogach reported size-tunable inorganic quantum dots, including CdSe and CdTe, which exhibited various luminescence colors and efficiencies.6,7 Scherf and co-workers investigated water-soluble organic NPs of polyfluorenes and poly(cyclopentadithiophene) derivatives with diameters of 50–250 nm, which tuned the emission color from green to red.8,9

The high performance of organic-based optoelectronic and biosensing devices has focused attention on organic NPs, as they are low-cost, and provided a large effective area, and low-temperature processing.10–18 Single crystalline organic NPs are a promising nanostructure for reducing grain boundaries and minimizing charge trapping sites, and for manipulation of the conducting or semiconducting nano-architectures.18,20 These NPs can enhance the efficiency of optoelectronic devices. The π–π interaction between organic molecules plays an important role for the crystallinity and physical shape of the organic nanostructures.20

Organic rubrene single crystals and thin films with a π-conjugated structure have been intensively studied as an excellent hole transport material in organic based optoelectronic and magnetic devices.21,22 Recent studies have reported the luminescence and charge transport characteristics, waveguiding, and spin transport of various rubrene nanostructures,22–24 however, the molecular design and nanoscale luminescence characteristics of the rubrene single NP have not been studied thoroughly.

Herein, we report on the fabrication and nanoscale luminescence characteristics of an isolated single NP of crystalline rubrene. Pristine rubrene (P-rubrene) NPs were prepared by a conventional reprecipitation method.25–28 A solvent-vapor annealing process on a selected substrate, as shown in Fig. 1(a), easily transformed the non-crystalline phase of the pristine rubrene NPs to the crystalline phase. We observed highly bright and sharp light emission of the laser confocal microscope (LCM) PL spectrum for the crystalline rubrene single NP, compared with the P-rubrene NP. The enhanced and sharp light emission of the crystalline rectangular rubrene (R-rubrene) and hexagonal rubrene (H-rubrene) single NP originated from the strong π–π interaction of rubrene molecules along the b-axis in the nano-sized single crystalline structure, which allows for an effective exciton transport (i.e., the long exciton diffusion length).29–33