RAPID COMMUNICATION

Nanophotonic droplet: a nanometric optical device consisting of size- and number-selective coupled quantum dots

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Abstract Although recent advances in fabrication technologies have allowed the realization of highly accurate nanometric devices and systems, most approaches still lack uniformity and mass-production capability sufficient for practical use. We have previously demonstrated a novel technique for autonomously coupling heterogeneous quantum dots to induce particular optical responses based on a simple phonon-assisted photocuring method in which a mixture of quantum dots and photocurable polymer is irradiated with light. The cured polymer sequentially encapsulates coupled quantum dots, forming what we call a *nanophotonic droplet*. Recently, we found that each quantum dot in the mixture is preferably coupled with other quantum dots of similar size due to a size resonance effect of the optical near-field interactions between them. Moreover, every nanophotonic droplet is likely to contain the same number of coupled quantum dots. In this paper, we describe the basic mechanisms of autonomously fabricating nanophotonic droplets, and we examine the size- and number-selectivity of the quantum dots during their coupling process. The results from experiments show the uniformity of the optical properties of mass-produced nanophotonic droplets, revealed by emission from the contained coupled quantum dots, due to the fundamental characteristics of our method.

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1 Introduction

Various fabrication technologies have been actively developed for realizing novel devices and systems that operate on the nanometric scale, and some of them have become commercially available [1–4]. Especially in the case nanophotonic devices [5] that operate based on optical near-field interactions between nanometric components, they must be fabricated by precisely combining and aligning nanometric components to exhibit the intended optical functions [6–9]. In order to develop the concepts and achievements of such nanometric devices and systems to a practical level where they can be employed in various applications, mass-production while maintaining uniform quality is essential.

Self-assembly is one promising method of realizing mass-production of nanometric devices [10–13]. Previously, we reported an all-autonomous technique for producing *nanophotonic droplets* [14]. A nanophotonic droplet is formed of coupled heterogeneous quantum dots (QDs) encapsulated by locally cured photocurable polymer. Encapsulation of selected micro- or nano-materials is an effective approach for preparing an isolated system from its surroundings, as well as realizing stability and durability [15–17]. During the process of fabricating nanophotonic droplets, incident light having a lower photon energy than the curing energy of the polymer is radiated. The incident light induces a phonon-assisted process [18–21], namely, multistep excitation, which cures the polymer via activated phonon levels. This process occurs only when heterogeneous QDs come close to each other. In this paper, we focus on the QD-coupling process and experimentally verified the size- and number-selectivity during the process due to the optical near-field interactions between QDs, which determines the uniformity of the optical properties

of mass-produced nanophotonic droplets. First, we briefly review the basics of the phonon-assisted photocuring method, whose details have been published in [14]. Then, we describe experiments conducted to reveal the characteristic features of the coupling process by measuring the optical properties of individual nanophotonic droplets.

2 Basics of producing a nanophotonic droplet

An optical near-field can be described with the concept of a dressed photon (DP), which is a quasi-particle representing the coupled state of a photon and an electron in a nanometric space [22]. A DP can excite a multi-mode phonon in a nanometric material and can then couple with this phonon [18–21]. The quasi-particle representing this coupled state has been named a dressed-photon-phonon (DPP). In our proposed method for producing nanophotonic droplets, we utilize the DPP for coupling heterogeneous QDs in a solution with a photocurable polymer and encapsulating them in the photocured polymer. In order to induce the photocuring process in a self-assembled manner, the mixture in the solution, in which QDs freely float, exhibiting Brownian motion, is irradiated with assisting light.

The principle of our proposed method is schematically shown in Fig. 1. We assume a mixture containing two types of QDs, QD_A and QD_B, and a photocurable polymer, and the mixture is irradiated with assisting light having photon energy $h\nu_{assist}$. The transition energies of QD_A and QD_B are $E_{A.bg}$ and $E_{B.bg}$, respectively, and the activation energy of the photocurable polymer is $E_{poly.act}$. When the energies satisfy the condition $E_{A.bg} < h\nu_{assist} < E_{poly.act} < E_{A.bg}$, the following process can be induced. If the numbers of QDs, or in other words, their volume densities, in the mixture are not sufficiently high and they rarely encounter each other, only QD_A spontaneously emits visible light by absorbing the assisting light. In this case, no subsequent physical or chemical reaction occurs. On the other hand, if the density is sufficiently high that the QDs can frequently encounter each other, multistep energy excitation of the photocurable polymer occurs due to DPP interactions between neighboring QD_A and QD_B, and the photocurable polymer is subsequently cured, as shown in the upper diagram in Fig. 1. Moreover, further irradiation with the assisting light induces multistep excitation of QD_B due to DPP interactions with the neighboring QD_A. Subsequently, QD_B spontaneously emits light with a higher photon energy than the assisting light, and the photocurable polymer in the surroundings is locally cured by absorption of the emitted light. As a result, the cured polymer encapsulates the coupled-QDs, preventing further combination or separation of the encapsulated QDs.
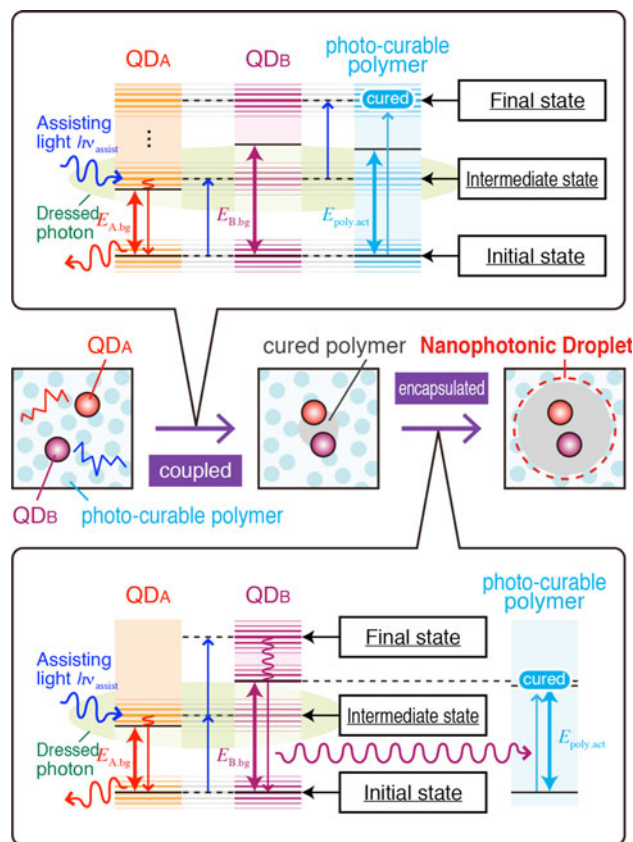

Fig. 1 Schematic diagram of process of fabricating a nanophotonic droplet based on phonon-assisted photocuring

Since the spatial distribution of the DPP energy generated on the surface of the QDs is expressed by a Yukawa function [23], the separation between the two QDs is theoretically defined by the Yukawa function. Moreover, the encapsulated coupled-QDs are necessarily composed of heterogeneous QDs, because the above sequence is induced only when QD_A and QD_B encounter each other. Descriptions of the electronic transitions via such a coupled state induced by the assisting light have been previously described in a recent report by the authors [14].

Here, we describe the size resonance effect of optical near-field interactions [24]. Because induced optical near-fields are localized around nanometric structures, and the scale of their spatial distribution is comparable to the size of the structure, as described by the Yukawa function [23], the energy of the optical near-field interactions between two nanometric structures is expected to be maximized when the sizes of the two structures are similar. From the theoretical formulation in [24], when two nanometric particles with diameters r_A and r_B come close to each other, as shown in Fig. 2a, the intensity of the size resonance effect, $I(d_{AB})$, between the two is given by

Fig. 2 **a** Schematic diagram of optical near-field interactions between two nanometric particles, and **b** intensity of optical near-field interactions between particles of various sizes. **c** Schematic diagram of size-selective coupling during fabrication of nanophotonic droplet due to the size resonance effect
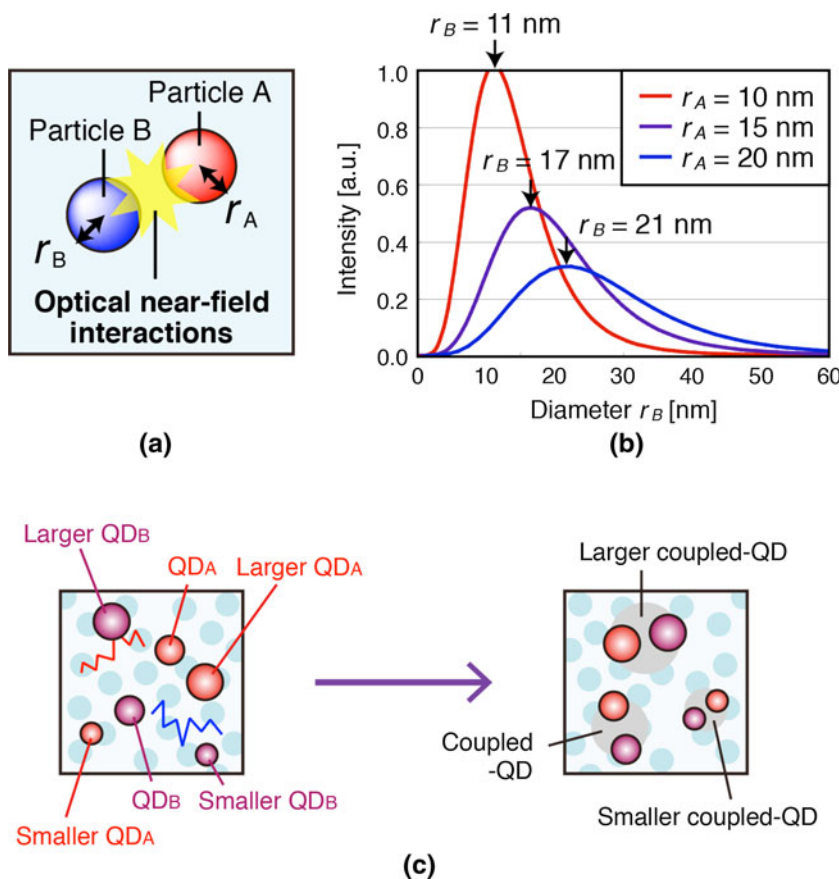
$$I(d_{AB}) = A \left[r_A^3 \left\{ \frac{r_B}{r_A} \cosh\left(\frac{r_B}{r_A}\right) - \sinh\left(\frac{r_B}{r_A}\right) \right\} \right.$$
$$\left. \times \left(\frac{1}{d_{AB}} + \frac{r_A}{d_{AB}^2} \right) \times \exp\left(-\frac{d_{AB}}{r_A} - 1\right) \right]^2, \quad (1)$$

where d_{AB} is the distance between the two particles, and A is a proportionality constant. Figure 2b plots the normalized intensity of the optical near-field interactions in the cases where $r_A = 10$, 15, and 20 nm. As shown, other particles with similar sizes, namely, $r_B = 11$, 17, and 21 nm, respectively, are likely to produce more intense interactions.

Because our phonon-assisted curing method is fundamentally induced by the optical near-field interactions between two heterogeneous QDs, QDs with similar sizes are assumed to be preferably coupled with each other due to this size resonance effect, as schematically shown in Fig. 2c. Moreover, encapsulation of the coupled-QDs begins almost as soon as the QDs are coupled. This means that each nanophotonic droplet is likely to contain only one pair of coupled-QDs. Because actual QDs necessarily exhibit a size distribution, and their size distribution causes inhomogeneous emission properties, such size- and number-selectivity of the QDs during the nanophotonic droplet fabrication process is expected to result in uniform

emission spectra and emission intensity of mass-produced nanophotonic droplets.

3 Experimental demonstrations

In order to demonstrate the uniformity of nanophotonic droplets, first we experimentally produced and extracted nanophotonic droplets by our proposed method. Specifically, as QD$_A$ and QD$_B$ in Fig. 1, we used solutions of CdSe-QDs and ZnO-QDs, which emit visible and ultraviolet (UV) light, respectively. These QD solutions were mixed with a UV-curable polymer and irradiated with visible assisting light whose photon energy was high enough to excite excitons in the CdSe-QDs but too low to excite excitons in the ZnO-QDs and the UV-curable polymer. Figure 3 shows the energy conditions for the following experiment. We used commercially available CdSe-QDs (Ocean Optics, *Evidot*) and ZnO-QDs prepared by sol–gel synthesis using photo-induced desorption [25]. The QD solutions were then dispersed in a UV-curable polymer (NORLAND, *NOA 65*) and irradiated with assisting light emitted from a 120-mW laser diode with a photon energy of 2.71 eV. These conditions fulfilled the previously described energy conditions for inducing the
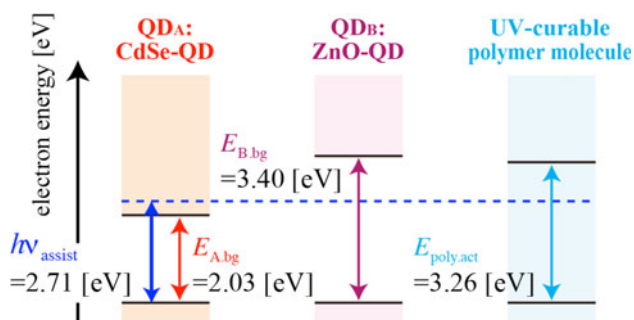
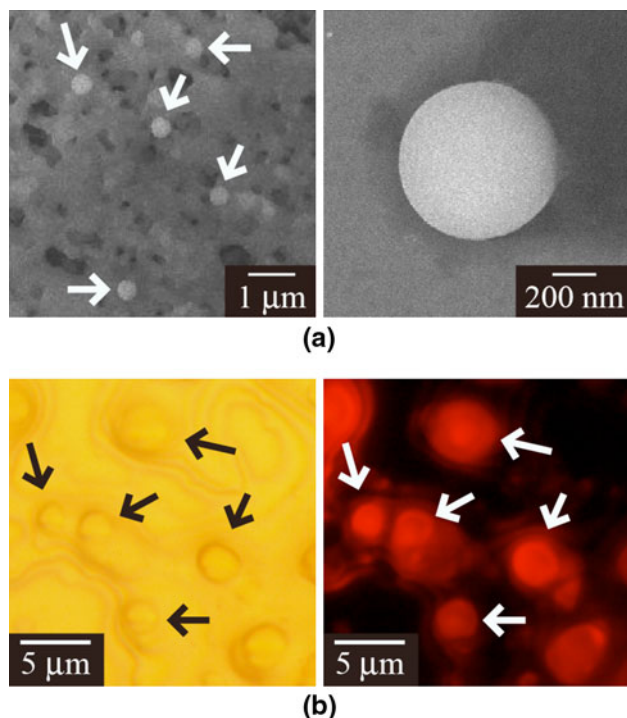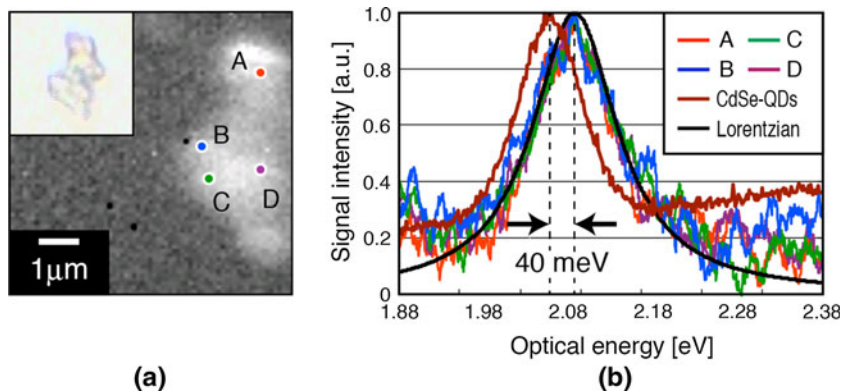**Fig. 3** Energy diagram of the experimental conditions

Fig. 4 a SEM images and **b** microscope images of mass-produced nanophotonic droplets

sequential process of the phonon-assisted photocuring method. The total amount of the mixed solution was limited to 50 μL to maintain spatially uniform illumination. This volume contained about 10^{14} CdSe-QDs and about 10^{12} ZnO-QDs.

Under these experimental conditions, the QDs can be assumed to encounter each other at a sufficiently high frequency to induce the phonon-assisted photocuring. After irradiation with the assisting light, the mixture was separated into cured and uncured materials by centrifugation at 10,000 rpm for 5 min. The extracted cured material, which was assumed to contain a large number of nanophotonic droplets, was dispersed in a toluene solution and uniformly spin-coated on a Si substrate. Figure 4a, b show SEM images and microscope images of materials irradiated with assisting light for 30 and 90 min, respectively. As shown, with the shorter irradiation time, nanophotonic droplets with quite similar sizes were successfully obtained. The diameter of each nanophotonic droplet was about 500 nm. With the longer irradiation time, the nanophotonic droplets increased in size to micrometer level and were successfully observed in the microscope images, as shown in Fig. 4b. The images on the left- and right-hand sides show a sample under white-light and UV-light illumination, respectively. As shown in the image on the right-hand side, each nanophotonic droplet exhibited emission from the contained CdSe-QDs.

In order to compare multiple emission spectra of individual nanophotonic droplets, we constructed a two-dimensional map of the emission spectra of samples obtained with a micro-spectrophotometer (NFGP-740, JASCO, Japan). Samples were irradiated by a laser diode with a photon energy of 3.06 eV. The spatial resolution of the experimental setup was expected to be less than 200 nm. Figure 5a shows a two-dimensional emission image of aggregated nanophotonic droplets. The inset represents a bright-field image under white-light illumination. The individual emission spectra of nanophotonic droplets A, B, C, and D indicated in Fig. 5a are respectively plotted in Fig. 5b.

Fig. 5 a Obtained emission image of aggregated nanophotonic droplets. **b** Emission spectra of multiple nanophotonic droplets, collectively observed emission spectrum of CdSe-QDs, and a Lorentzian fitted curve

As shown, the heights and widths of the emission spectra are quite similar to each other. Because they can be simply fitted by a single Lorentzian, which is generally applied to approximate the emission spectrum of a single illuminant, it is considered that the nanophotonic droplets contain single CdSe-QDs of similar size and coupled ZnO-QDs. This demonstrates the uniformity of the optical properties of mass-produced nanophotonic droplets.

We also measured the collectively observed emission spectrum of multiple CdSe-QDs, as shown in Fig. 5b. The sample was prepared by mixing a solution of CdSe-QDs and a UV-curable polymer, and was directly spin-coated on a substrate without any irradiation with assisting light. There was a 40 meV difference between the peak optical energy in the spectra of the individual nanophotonic droplets and the collective CdSe-QDs. Such a large difference is due to not only re-absorption of emission within the collective CdSe-QDs, but also size-selectivity during the coupling process between CdSe-QD and ZnO-QD. The result indicates that ZnO-QDs preferably coupled with *smaller* CdSe-QDs in the mixture and revealed such uniformity in their emission spectra.

4 Summary

In this paper, we described the uniformity of the optical properties of mass-produced nanophotonic droplets, made possible by a novel fabrication process based on optical near-field interactions between nanometric components. From the results of our experimental demonstrations, we verified that such uniformity was physically ensured by the size-selectivity during the QD-coupling process, and that each nanophotonic droplet contained the same number of QDs, exhibiting the expected homogeneity. These findings show the fundamental features of our proposed method, where we can obtain a large number of nanophotonic droplets with homogeneous optical properties with an all-autonomous fabrication process. Our method can be easily applied to various applications where novel nanophotonics and nanotechnologies are required for further practical development.

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