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Self-assembly method of linearly aligning ZnO quantum dots for a nanophotonic signal transmission device

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We report a self-assembly method that aligns nanometer-sized quantum dots (QDs) into a straight line along which photonic signals can be transmitted by optically near-field effects. ZnO QDs were bound electrostatically to DNA to form a one-dimensional QD chain. The photoluminescence intensity under parallel polarization excitation along the QDs chain was much greater than under perpendicular polarization excitation, indicating an efficient signal transmission along the QD chain. As optical near-field energy can transmit through the resonant energy level, nanophotonic signal transmission devices have a number of potential applications, such as wavelength division multiplexing using QDs of different sizes. © 2010 American Institute of Physics.

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Innovations in optical technology are required for the continued development of information processing systems. One potential innovation, the increased integration of photonic devices, requires a reduction in both the size of the devices and the amount of heat they generate. Chains of closely spaced metal nanoparticles that can convert the optical mode into nonradiating surface plasmonic waves have been proposed as a way to meet these requirements.^{1,2} However, one disadvantage is that they cannot break the plasmon diffraction limit. To overcome this difficulty, we developed nanophotonic signal transmission (NST) devices consisting of semiconductor quantum dots (QDs).^{3–5} These NST devices operate using excitons generated in the QDs by optical near-field interactions between closely spaced QDs as the signal carrier. The exciton energy is transferred to adjacent QDs through resonant exciton energy levels, and therefore the optical beam spot may be decreased to the size of the QD. Moreover, NST devices using semiconductor QDs have higher transmission efficiency because QDs hardly couple with the lattice vibrational modes as opposed to transmission in metallic waveguides. This lattice vibration is the principal cause of large propagation losses in plasmonic waveguides. Here we report a self-assembly method that aligns nanometer-sized QDs into a straight line along which photonic signals can be transmitted by optically near-field effects.

The NST device fabrication process requires the following:

- (A) Small size dispersion of QDs: it is estimated that to fabricate an NST device consisting of 5 nm QDs and an efficiency equivalent of 97%, the size dispersion must be as small as ± 0.5 nm.³
- (B) Subnanometer scale controllability in the separation between QDs: because the optical near-field coupling efficiency between adjacent QDs is determined by a

Yukawa type function,⁶ the separation between QDs should be controlled to a subnanometer scale.

To meet these requirements, we developed a new technique for positioning and aligning QDs that yields precise separation. Figure 1 illustrates our approach to a self-assembling NST device with angstrom-scale spacing controllability among QDs using silane-based molecular spacers and deoxyribonucleic acid (DNA).^{7,8} First, ZnO QDs 5 nm in diameter were synthesized using the sol-gel method.^{9,10} Typical transmission electron micrographic (TEM) images of synthesized ZnO dots are presented in Figs. 2(a) and 2(b). The dark areas indicated by the dashed ellipses correspond to the ZnO QD. These images reveal lattice spacing matches for the c-plane (0.26 nm) and m-plane (0.28 nm) of wurtzite ZnO. These results confirmed that the fabricated ZnO QDs had high-quality single-crystal crystallinity. An average ZnO QDs diameter of 5.2 nm with a standard deviation (σ) of 0.5 nm was determined from TEM images [Fig. 2(c)] and meets the first requirement (A).

Second, the surfaces of QD were coated with a silane coupling agent $\text{N}^+(\text{CH}_3)_3(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ with 0.6 nm in length. To avoid particle aggregation, we added small

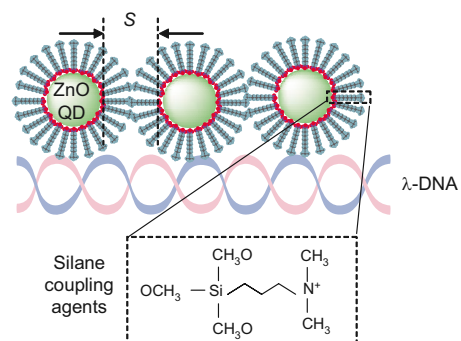


FIG. 1. (Color online) Schematic of ZnO QD alignment along the λ DNA. S: separation between QDs.

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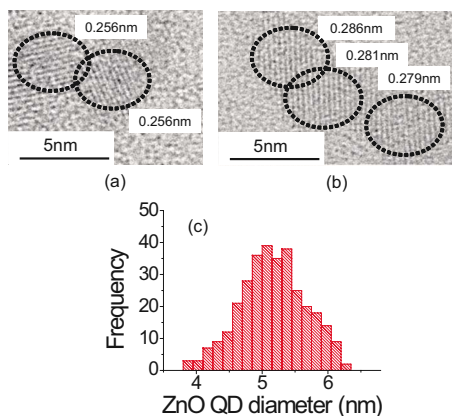


FIG. 2. (Color online) TEM analysis of fabricated ZnO QDs. [(a) and (b)] Typical TEM pictures of the ZnO QDs. (c) ZnO QD diameter distribution.

amounts of the agent into the ZnO QD colloidal dispersion. The agent maintains the spacing between QDs and, because of its cationic nature, acts as an adhesive for the anionic DNA. Third, we used λ DNA (number of base pairs = 48 000, stretched length = 16.4 μm) as the template to align the QDs so that the QDs were self-assembled onto the DNA by electrostatic interactions when they were mixed. As shown in the TEM image [Fig. 3(a)], dense packing of the ZnO QDs along the DNA was realized, in which the diameter of the DNA with the QDs was 15 nm. Considering a QD size of 5 nm and the DNA diameter of 2 nm, four QDs were attached around the DNA [see Figs. 3(b) and 3(c)]. The 1.2 nm separation between QDs (S) was determined from the TEM image [Fig. 3(d)] and was in good agreement with twice the length of the silane coupling agents. Because the length of the silane coupling agents can be controlled by changing the number of CH_2 by 0.15 nm, this technique meets the second requirement (B). Despite the electrostatic repulsion between ZnO QDs, such high-density packing is due to the quaternary ammonium group of the silane coupling agent.⁷ Quaternary ammonium groups and these QDs have highly condensed positive electrical charges on their particle surfaces. Because of these condensed charges, the QDs were densely adsorbed on the oppositely charged surfaces when their intervals were fixed by the stabilizer length.

To observe the optical properties of the NST, we stretched and straightened the QD-immobilized DNA on the

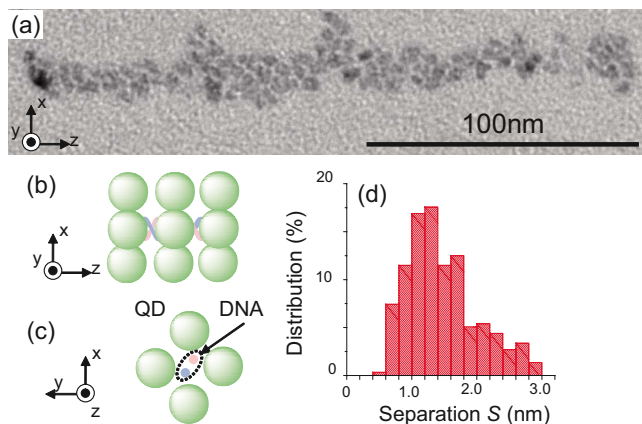


FIG. 3. (Color online) TEM analysis of aligned ZnO QDs. (a) TEM image of the aligned ZnO QDs. [(b) and (c)] Schematics of the QD alignment along the DNA. (d) Separation (S) distribution.

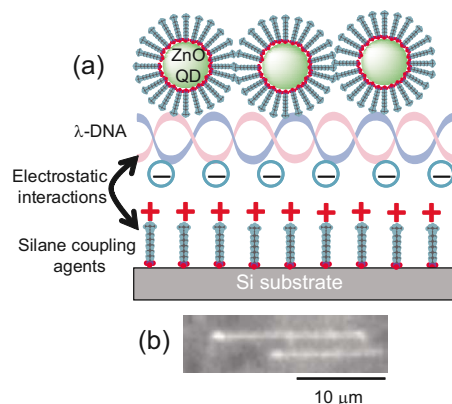


FIG. 4. (Color online) Schematic of the molecular combing technique. (a) Schematic of the alignment of the DNA with QDs on the cationic silicon substrate. (b) Charge-coupled device image of the stretched λ DNA.

silicon substrate using the molecular combing technique [Fig. 4(a)].¹¹ First, the silicon substrate was terminated with the silane coupling agent so that the anionic DNA was adsorbed on the cationic silicon substrate. Second, the solution including the DNA and the QDs was dropped onto the cationic silicon substrate. Finally, the glass substrate was slid over the droplet. To check the alignment of DNA-QDs alignment, we obtained an emission image of the cyanine dye attached to the DNA using its 540 nm emission peak under halogen lamp illumination. As shown in the optical image taken with a charge-coupled device camera [Fig. 4(b)], the DNA with QDs stretched in the direction determined by the slide direction of the glass substrate; also, these stretched DNA were found to be isolated.

Using the linearly aligned ZnO QDs, we evaluated the photoluminescence (PL) polarization dependence. A fourth-harmonic of a Q-switched Nd:YAG laser (neodymium-doped yttrium aluminum garnet; $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$ laser, $\lambda = 266$ nm) with a spot size of approximately 2 mm was used to excite the ZnO QDs at various polarization angles [Fig. 5(a)]. From the polarization dependence of the PL at a wavelength of 350 nm [Fig. 5(b)], corresponding to the ground state of 5 nm ZnO QDs, stronger PL emission was obtained by exciting the parallel polarization along the QD chains (E_0) than was obtained under the perpendicular polarization [E_{90} ; Fig. 5(c)]. Since the decay time of ZnO QDs is more than 20 times longer than the energy transfer time to adjacent QDs,¹⁰ it is possible that the dipoles between adjacent QDs were coupled by an optical near-field interaction, indicating that the signals were transmitted through the QD chain. Furthermore, QD chains have great dipolar strength [see the inset of Fig. 5(c)] that can be realized when the QDs are coherently coupled.^{12,13} If M QDs are coherently coupled and the coherent length along the z -axis is N times greater than that along the x -axis, the equivalent total dipolar strength is given by $Me \times d$ [E_{90} ; see Fig. 5(d)] and $Me \times Nd$ [E_0 ; see Fig. 5(e)], where e is the electrical charge excited in the QD and d is the coherent length along the x -axis, which is equivalent to the width of the QD chain. The resulting emission intensities are $(Me \times d)^2$ and $(Me \times Nd)^2$ for E_{90} and E_0 , respectively. Therefore, we obtained N^2 times greater PL intensity with E_0 than with E_{90} . To evaluate the number of coherently coupled QDs, N , we fit the polarization intensity dependence $\text{PL}(\theta)$ using

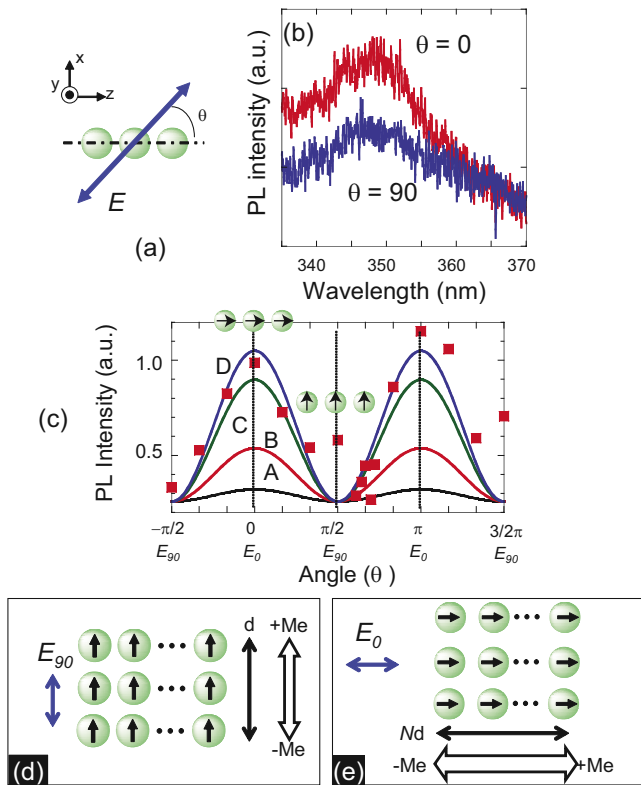


FIG. 5. (Color online) Polarization dependence of the linearly aligned QD chain. (a) Incident light polarization dependence of PL intensity. θ : Polarization angle with respect to the direction along the QD chains (x -axis). (b) Typical PL spectra obtained at $\theta=0$ and 90° . (c) Incident light polarization dependence of the PL intensity obtained at $\lambda=350$ nm. Curves A to D correspond to $N=3, 6, 9$, and 10 , respectively. Schematics of the equivalent total dipole strength under (d) E_{90} and (e) E_0 .

$$PL(\theta) = k(\sin^2 \theta + N^2 \cos^2 \theta) + \text{const.}, \quad (1)$$

where k is a proportionality constant. As shown by the solid curves in Fig. 5(c) (curves A to D correspond to $N=3, 6, 9$, and 10 , respectively), the polarization dependence of the PL intensity was fitted using Eq. (1), and the value of N was estimated to be 10 , indicating that the coherent length along the z -axis was ten times greater than the width of the QD chain. Since the QD chain was 15 nm wide [see Fig. 3(a)],

the coherent length along the QD chain was 150 nm. This value is five times larger than that in bulk ZnO.¹⁴ This large coherent length along the QD chains originates from the reduction in phonon scattering in the QDs due to the decrease in the propagation length through ZnO for QDs.

In conclusion, we developed a self-assembly method for linearly aligning QDs to realize a NST device. The polarization-dependent PL from the QD chain revealed that the coherent length along the QDs chain was 150 nm, indicating efficient signal transmission through the QD chain. As optical near-field energy can transmit through the resonant energy level, NST devices have a number of potential applications, such as wavelength division multiplexing using QDs of different sizes.

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