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Single Quantum Dots as Local Temperature Markers

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ABSTRACT

This work describes noncontact, local temperature measurements using wavelength shifts of CdSe quantum dots (QDs). Individual QDs are demonstrated to be capable of sensing temperature variations and reporting temperature changes remotely through optical readout. Temperature profiles of a microheater under different input voltages are evaluated based on the spectral shift of QDs on the heater, and results are consistent with a one-dimensional electrothermal model. The theoretical resolution of this technique could go down to the size of a single quantum dot using far-field optics for temperature characterizations of micro/nanostructures.

When the characteristic dimension of functional structures reduces down to the nanometer range, it becomes extremely challenging to measure their temperature using conventional techniques either in the contact or in the noncontact modes due to insufficient spatial resolution.[1,2] For example, a thermocouple has a spatial resolution of ∼100 μm and a temperature-sensitive paint of ∼1 μm.[3,4] Recently, submicrometer, high-spatial-resolution temperature sensing using near-infrared imaging has been demonstrated.[5] We propose in this work to use semiconductor nanocrystalline particles or quantum dots (QDs), by virtue of their small sizes and favorable photostability, for temperature markers providing far-field optical readouts for micro- and nanostructures. These luminescence-based sensors are sensitive and have great potential in many research areas.[6−8] Previous works have shown that the spectroscopic characteristics for an ensemble of CdSe QDs shift with temperature.[9−12] It is not apparent, however, if individual QDs can provide a temperature readout through changes in their spectral characteristics, in particular, in view of their complicated photoemission behavior at the single-particle level.[13−15] In this Letter, we report the observation that the time-averaged emission spectrum from individual QDs is sensitive to temperature changes in the biologically compatible range and demonstrate its application to noncontact, local temperature sensing of microelectromechanical system (MEMS) heaters.

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Figure 1 shows schematically how CdSe QDs with a nominal diameter of ∼7−12 nm (core and shell) can be used to detect temperature changes in a noncontact mode. The commercially available water-soluble CdSe quantum dots with an emission maximum at ∼655 nm (Qdots/Invitrogen) came encapsulated by a ZnS shell, coated with a layer of organic polymer, and conjugated with streptavidin. The stock QD solution was diluted in phosphate-buffered saline (PBS) to ∼0.5 pM. The concentration of the QD sample was kept low to optically resolve individual dots. 20 μL of this dilution was sandwiched between two 24 × 40 mm² glass cover slips. After a 10-min period of incubation at 100 °C for drying QD solution, the cover slips were separated and 10 μL of polydimethylsiloxane (PDMS, Sylgard 184) was added on one cover slip to fix the position of QDs. Afterward, a 18 × 18 mm² glass cover slip was covered on the sample and sealed by nail polish on the edges. Typically, about 10 single QDs were recorded in a field of view, 80 × 10 μm², in our optical setup. The sample was mounted on a sample holder whose temperature was regulated by a water bath. A thermocouple (5SC-TT-K-36-36; Omega Engineering, Inc.) was taped onto the top of a small glass cover slip next to the observation point to monitor the device temperature. A 532-nm continuous-wave laser (Compass 315M-100, Coherent) was used to excite single QDs through a microscope (IX71, Olympus). A total internal reflection fluorescence (TIRF) objective (100× with a numerical aperture of 1.45) was used to acquire the image and spectrum of individual quantum dots. The emission from each QD was collected through a dichroic mirror (560dclp, Chroma) to reject the excitation light. The spectrally filtered emission was further

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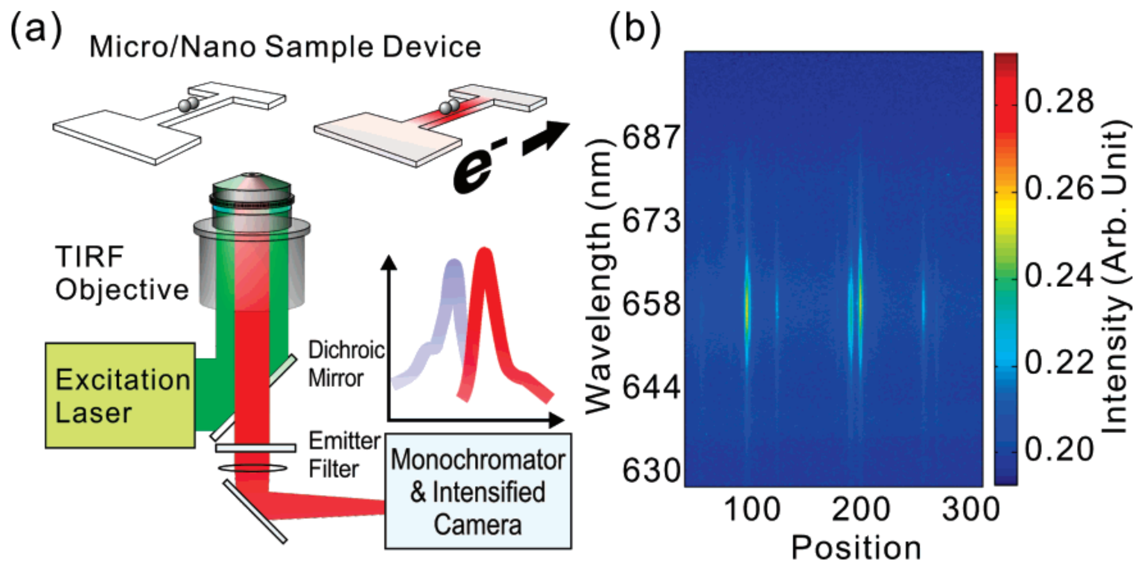

Figure 1. (a) Schematic diagram of noncontact temperature characterization using quantum dots through emission spectral shifts. (b) Representative spectrum-position image containing several single QDs.

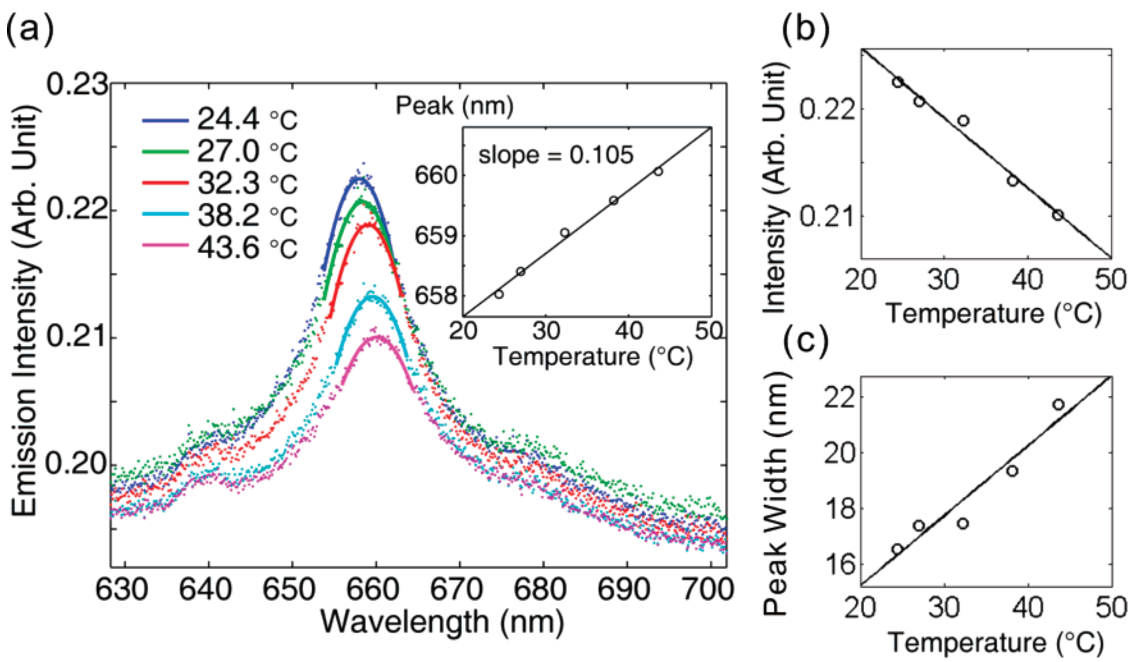

Figure 2. Temperature-dependent spectral shifts of a single QD from 24.4 to 43.6 °C. The raw spectra and Gaussian fits are shown as dots and solid lines, respectively. Insert: Wavelength shift is a linear function of temperature in this temperature range. (b) Plot of the average emission intensity as a function of temperature. (c) Spectral width as a function of temperature.

dispersed by a spectrograph (SP2150i, grating 600 g/mm blazed at 500 nm for single QDs spectra measurement, grating 1200 g/mm blazed at 500 nm for MEMS microheater temperature profile measurement; Princeton Instruments/Acton) and imaged by an intensified camera (Cascade 512B, Roper Scientific). The entrance slit of the spectrograph also served as a means to minimize the influence of other QDs outside the centerline region.[16] The central wavelength of the spectrograph was set to 655 nm.

To characterize the spectral shift of individual QDs and to eliminate the blinking effects, 100 frames were acquired with a 2 s/frame exposure time at each temperature. Figure 2 displays representative emission spectra of a single QD when the substrate temperature was increased from 24.4 to 43.6 °C. Using this QD as an example, one observes that the peak wavelength of a single QD exhibits a red-shift to longer wavelengths as the temperature increases. The temperature sensitivity is ∼0.1 nm/°C, consistent with previous bulk measurements, which gave an expected ∼0.093 nm/°C dependence at this temperature range.[12] Temperature-dependent shifts in the wavelength has been understood in terms of temperature-dependent dilatation of the lattice and electron−lattice interaction.[17] The average emission intensity and the spectral width were found to decrease and broaden at higher temperatures (cf. Figure 2b,c). They can be attributed to escalated interaction between exciton and longitudinal optical phonon in the CdSe core at elevated temperatures, resulting in enhanced nonradiative decay.[10,11,18−21] Therefore, this

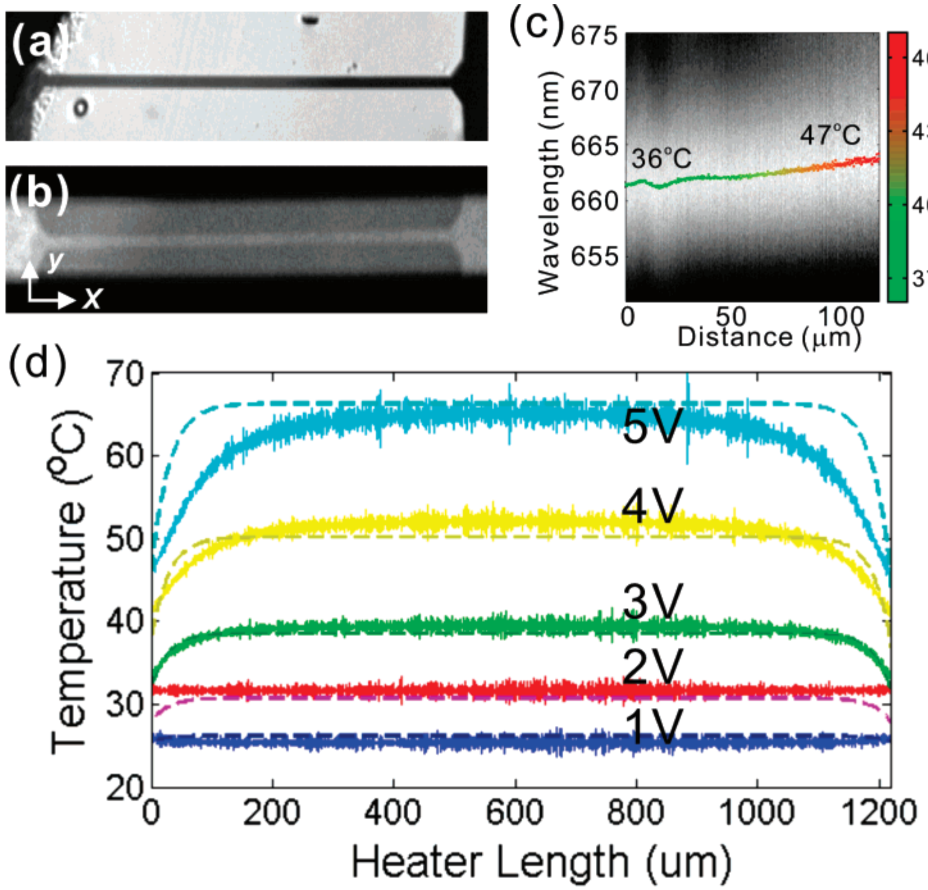

Figure 3. (a) Wide-field image of a fabricated aluminum microheater. (b) Fluorescent image of the microheater coated with CdSe QDs. (c) QD spectrum-position image of the red rectangle indicated in (a). Pseudocolor indicates the temperature differences. (d) Temperature profiles across the heater measured by QD spectral shift (solid lines). Temperature profiles calculated using an analytical model (dash lines).

experiment demonstrates that individual QDs are capable of sensing temperature variations and reporting temperature changes remotely through optical readout.

During our investigation, however, we also observed that the peak emission wavelength varied from dot to dot. For instance, statistical analysis on peak emission wavelength of 71 single QDs at room temperature gives a standard deviation of 2.4 nm, with a mean value of 659 nm. QDs with the same peak emission wavelength can exhibit different temperature-sensing behavior, however. The variation is likely due to a distribution in the size and shape of individual wet-chemistry-synthesized QDs.[22,23] The observation indicates that it may not be advisable to measure absolute temperatures (instead of relative temperature change) based on results from a single QD. Yet, the ensemble-averaged temperature-dependent spectroscopic characteristics appear to be reproducible.[9−12] This consideration motivated us to ask the question about the number of particles it requires to give a reliable temperature reading. To address this question, we first performed the bootstrap statistical analysis[24] on single-particle data to investigate the number of particles needed for their spectral mean to converge to the bulk results. We found that the relative deviation of the averaged spectral mean scales as $N^{-1/2}$, where N is the number of particles being considered: $|\langle\lambda\rangle_N - \langle\lambda\rangle_{\text{ensemble}}|/\langle\lambda\rangle_{\text{ensemble}} \approx A/\sqrt{N}$, where $A = 5.28 \times 10^{-3}$ at room temperature (22 °C). Using this empirical relation and the ∼0.1 nm/°C temperature-dependent spectral shift, we can estimate the number of particles needed to achieve a certain precision in optical temperature readout. For example, it will take about 1200 particles to make a temperature measurement with 1 °C precision. TEM measurements of more than 200 QD/Streptavidin conjugates showed an average length and width of 11.9 ± 2.3 nm and 6.95 ± 0.88 nm, respectively.[15] We estimate that it will require a surface area of ∼355 nm in diameter to accommodate these particles. This analysis suggests that it is possible to measure temperatures with optical spatial resolution. As a demonstration, we implement these ideas to a MEMS application where the remote sensing of local temperature with good spatial resolution is very challenging.

The MEMS microheater was made of aluminum with dimensions of 1200 × 40 × 0.1 μm^3, fabricated on top of a Pyrex wafer by evaporation and lift-off processes. It has two 1.5-mm-diameter circular contact pads, where the wires were connected out using conductive epoxy (ITW Chemtronics). Afterward, 3 μL of 200 pM CdSe QD solution was applied and dried in air. Parts a and b of Figure 3 show respectively the wide-field image and the fluorescent image of the microheater coated with CdSe QDs under low magnification. For the noncontact temperature measurement, a 60× air objective was used. When projected on the camera (512 ×

512 pixels), each spectrum-position image corresponded to 118 μm in length along the heater. Therefore, each pixel along the abscissa (along the heater) in the spectral image corresponded to a physical width of ~230 nm on the heater. Experimentally, 12 images were required to cover the entire 1.2-mm heater and the overlapped portions between consecutive images were averaged in the data analysis. The entrance slit of the spectrograph placed at the image plane of the microscope was set to 30 μm wide, corresponding to a 500-nm-wide stripe along the axis perpendicular to the heater. Thus each spectrum corresponds to QDs from the 500 nm by 230 nm image area at the sample. The QD emission from each area is spectrally resolved by the spectrograph so that the peak emission of the spectrum reports the local temperature. For each set of spectral recording, 10 frames of spectral image were acquired with 1 s/frame exposure time. The temperature of the microheater was adjusted by applying different voltages. The spectral data were collected after the heater reached steady state. The experimentally measured temperature profile was obtained based on the calibration results from the aforementioned single QD experiment. A representative QD spectrum-position image is shown in Figure 3c. The dots indicate the peak wavelengths of the spectra from a Gaussian fit and are color coded to reflect the corresponding temperatures. After combining the spectrum-position images and removing a low-frequency interference pattern (at ~0.03 μm^{-1} due to the excitation laser) using a band-pass Fourier filter, we were able to reconstruct the temperature profile along the aluminum heater, shown in Figure 3d (solid lines).

Analytically, temperature characteristics of the microheater are determined by various parameters such as current density, geometry, and thermal properties including temperature coefficient of the resistivity. The steady-state temperature profile of the attached, line-shape microheater has been developed previously based on a one-dimensional, electrothermal model[25] by assuming the two big contact pads remain at ambient temperature during experiments. The calculated temperature profiles across the microheater under different applied voltages are plotted (dash lines) in Figure 3d, along with the QDs temperature profile extracted from the spectrum measurements (solid lines). It is observed that the two independent methods predict similar temperature results qualitatively and quantitatively. Major discrepancy comes at the two ends, where QDs measurements indicate temperature higher than the ambient temperature as the contact pads could heat up a bit as predicted previously.[26]

The spectral shift of a single quantum dot was characterized as 0.1 nm/°C at room-temperature range, and the temperature profiles of a microheater was reconstructed using spectral shift of QDs. Both experimental and simulation results show good consistency with a 230-nm spatial resolution that is limited by the optical setup. Furthermore, empirical relations and statistical analyses conclude that about 1200 particles are needed to achieve 1 °C precision in optical temperature readout. As such, this technique has the potential to be applied to noncontact micro/nanotemperature measurements.

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