Luminescence of Individual Porous Si Chromophores

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We spatially isolate and detect the luminescence from individual porous Si nanoparticles at room temperature. Our experiments show a variety of phenomena not previously observed in the emission from porous Si including a distribution of emission wavelengths, resolved vibronic structure, luminescence intermittency, and irreversible photobleaching. Our results indicate that the emission from porous Si nanoparticles originates from excitons in quantum confined Si, and is strongly mediated by the surface of the quantum dot.   [S0031-9007(98)06403-5]

Visible light emission from Si via anodic etching in aqueous HF has stimulated tremendous interest over the past several years due to its potential application in optoelectronic devices and its ability to be integrated with current Si processing technology [1–4]. Despite the wide variety of spectroscopic techniques (absorption, luminescence, Raman and infrared spectroscopies) applied to porous Si, a detailed understanding of the photoluminescence, has yet to be achieved [3–7]. Principal reasons for this include the large heterogeneity in porous Si samples and the poor spatial selectivity of the spectroscopy techniques which average over large sample volumes [4]. In our experiments, we spatially isolate and detect emission from single porous Si nanoparticles. We observe a variety of phenomena not previously observed in the luminescence from porous Si including a distribution of luminescence wavelengths, resolved emission peaks, discrete jumps in intensity, luminescence intermittency (blinking), and irreversible photobleaching. Each of these phenomena is similar to phenomena observed in the emission of single CdSe nanocrystals [8,9], single trapped ions in the gas phase [10], and single dye molecules [11–16], suggesting that they arise from individual quantum systems.

Our experimental approach combines the techniques of single particle spectroscopy [8,9] and shear force microscopy [17]. Samples of well-separated porous Si nanoparticles were prepared by spin casting a 30 μl aliquot of approximately 1 nM colloidal porous Si onto a glass coverslip. Colloidal porous Si samples were prepared from bulk porous Si using the method of Heinrich *et al.* [18]. Figure 1 shows a typical luminescence image of a sample of porous Si nanoparticles containing several well-separated 300 nm spots. Samples were imaged in the far field using a laser scanning confocal microscope described in detail elsewhere [16]. In all of the experiments, the 514 nm line of an Ar$^+$ laser was used as the excitation source. A key feature of our apparatus is the ability to acquire total emission intensity and emission spectra simultaneously.

Our dispersed samples displayed a variety of particle sizes but only those particles that had a spot size of 300 nm

(the resolution limit of our microscope) were selected for study. In order to determine the size of the particle more quantitatively, we applied shear force microscopy, an analog of atomic force microscopy (AFM) [10]. In this technique, a tapered optical fiber tip (with tip size of approximately 300 nm) was used to track the surface of the nanoparticle. Assuming a roughly spherical particle it is possible to determine the size of an individual particle from the height of the image [19]. The nanoparticles studied in the experiments discussed here ranged between 5 and 20 nm in size.

During imaging it was observed that the fluorescence emission of many of the Si nanoparticles appeared to blink "on" and "off" during the course of a scan [as illustrated in the image of Fig. 1(B)]. The blinking behavior was examined more closely by positioning the excitation beam over a single particle and collecting the emission intensity vs time (intensity time course). In addition to blinking "on" and "off," many of the nanoparticles also emitted at discrete intensity levels as illustrated in Fig. 2(A). In Fig. 2(A), there are four distinct intensity levels of approximately 600, 400, 200, and 25 counts/s (the background level). We attribute this behavior to emission from a combination of three chromophores with the above intensity levels corresponding to emission from 3, 2, 1, or no chromophores, respectively. Based on previous measurements of luminescence lifetimes and efficiencies in porous Si samples, the signal level of 200 counts/s is consistent with emission from a single chromophore. The luminescence lifetime of porous Si samples with peak emission near 2.1 eV (600 nm) has been shown to be of the order of 1 μs, with emission efficiency of the order of 1% [4]. With our detection efficiency of 10%, a maximum count rate of 10^3 counts/s is expected for a saturated transition.

The rapid jump from the background signal to 600 counts/s observed in Fig. 2(A) suggests the possibility of coupling between chromophores in the particle. In general, we observe a decrease in the "on" times with increasing excitation intensity suggesting a light induced mechanism. The time course of Fig. 2(B) shows only one "on" level indicative of either one single chromophore
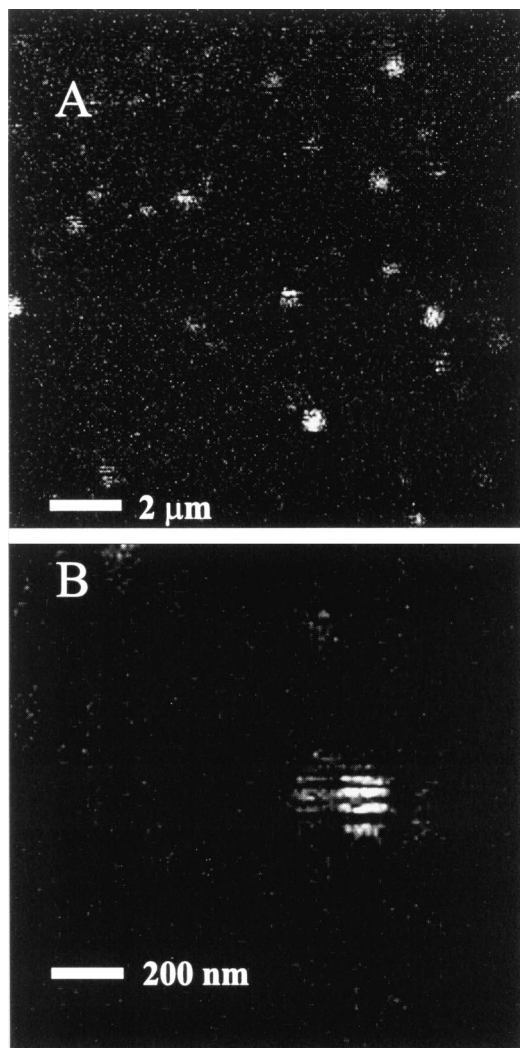
FIG. 1. Confocal fluorescence images of two representative nanoparticle samples. The 15×15 μm image in (A) was acquired at a rate of 2 lines per sec (256 pixels per line) with a 514.5 nm excitation source. The horizontal dark lines faintly visible on the fluorescing nanoparticle spots represent "on/off" blinking on the time scale of the scan. In (B), a higher magnification (2×2 μm) image of one such blinking particle is shown which clearly exhibits both fluorescence periods and dark periods during acquisition.

or two or more strongly coupled chromophores. The time course of Fig. 2(C) is from a very large (>500 nm) particle. No blinking is observed for large particles as expected for an ensemble of chromophores. The gradual decrease in fluorescence intensity observed in Fig. 2(C) is attributed to an irreversible photo-oxidation of the particle similar to that which occurs in bulk porous Si [4].

The blinking behavior observed in our porous silicon nanoparticles (the length of the "off" periods, the intensity dependence, and the photobleaching time) is strikingly similar to that observed in the room temperature luminescence from single CdSe quantum dots [8,9]. This suggests that the mechanism used to explain the blinking observed in CdSe quantum dots could also describe the blinking we observe in our porous Si nanoparticles. In this model,

the "off" state is characterized by an ionized quantum dot. Initially the exciton is trapped near the surface of the quantum dot. An additional exciton is quenched nonradiatively by energy transfer to the surface-trapped exciton in an Auger-type process eventually ionizing the chromophore. Subsequent excitations in the quantum dot are then quenched nonradiatively by releasing energy to this free carrier. The "on" state returns once the ionized quantum dot is neutralized. An important consequence of this model is that it implies a strong coupling between excitons and the surface of the quantum dot. It is also worth noting that the trapping of excitons by surface states has been used
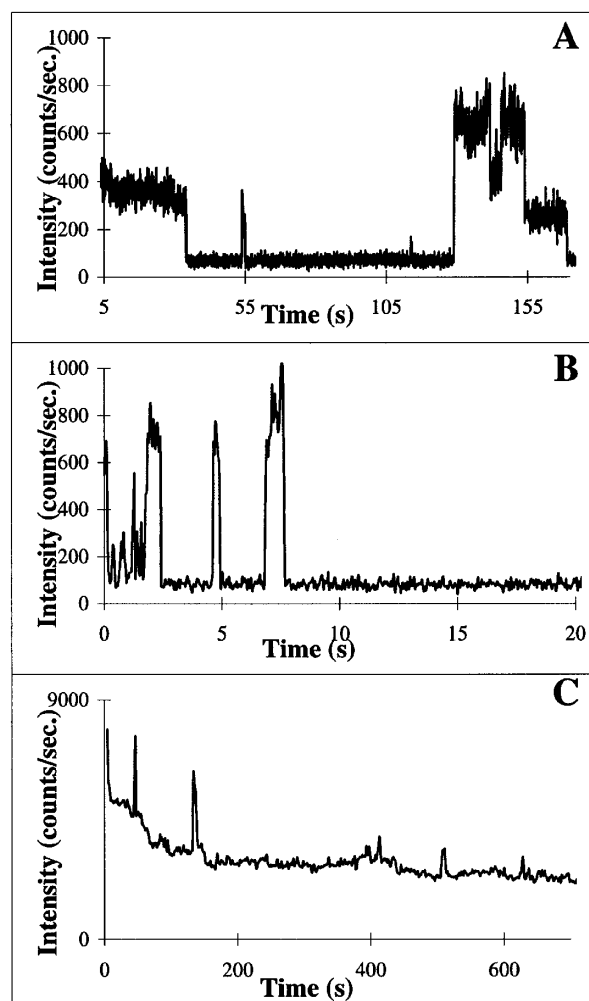

FIG. 2. Emission intensity vs time data for three porous Si particles. In (A), discrete intensity jumps in the emission of a $\sim$10 nm nanoparticle indicates the presence of three chromophores. An intensity of $\sim$600, 400, and 200 photon counts implies that 3, 2, or 1 chromophores are emitting, respectively. A signal on the order of $\sim$25 counts is representative of the background. In (B), rapid blinking is observed from only one intensity level indicating the possibility of a single chromophore. In (C), emission from a large particle (>500 nm) is collected over 12 min demonstrating the gradual decrease in intensity due to photo-oxidation similar to that observed for bulk porous Si (see Ref. [4]). Note the lack of "on-off" behavior in this ensemble of chromophores.
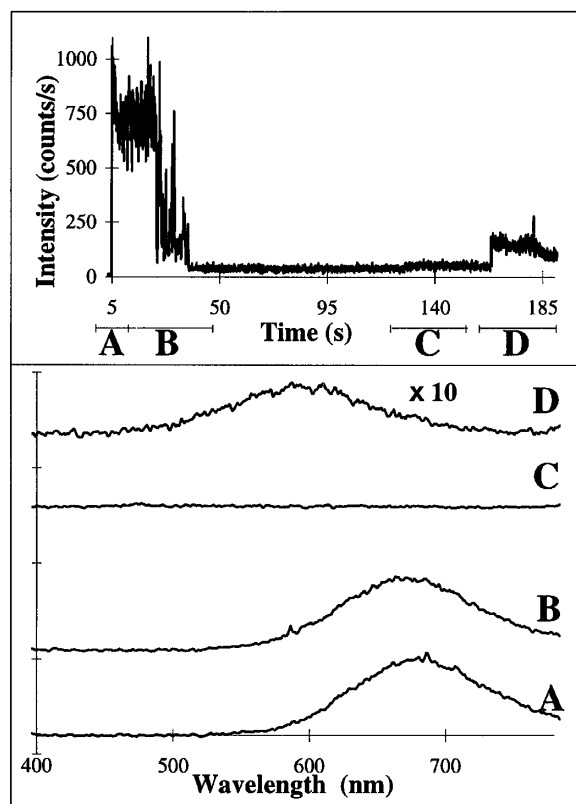
FIG. 3. Emission intensity vs time data and corresponding fluorescence spectra of a single porous Si particle ($<$50 nm). The spectral intensities of (A), (B), and (C) are shown on the same intensity scale while that of (D) is multiplied by a factor of 10 to help illustrate the large blueshift. Spectrum (A) was collected using a 30 sec integration period while (B), (C), and (D) were all collected over 60 sec integration periods. The shift in peak wavelength between (A), (B), and (D) shows the strong correlation between emission intensity and emission wavelength. This indicates that at least three chromophores are emitting in the particle as described in the text. During time interval (C) none of the chromophores are emitting.

previously to explain dynamics in porous Si [20–22], but there has been no direct evidence for such a model.

The emission spectra in Fig. 3 were acquired simultaneously with the intensity time course also shown in the figure. The intensity of the spectra in Figs. 3(A), 3(B), and 3(C) are shown on the same scale while that of Fig. 3(D) is multiplied by a factor of 10 to help illustrate the large spectral shift. A probable explanation for the behavior demonstrated in Fig. 3 is that there are three chromophores contributing to the total emission of the nanoparticle; one weak emitter centered at $\lambda_{max} \approx$ 575 nm [see Fig. 3(D)], and two stronger ones emitting near $\lambda_{max} \approx$ 650 nm and $\lambda_{max} \approx$ 680 nm [Figs. 3(B) and 3(A)], respectively.

The lineshapes of each of the spectra of Fig. 3 are analogous to that observed for bulk porous Si and for large porous Si particles [Fig. 4(A)] exhibiting no discernible structure. This broad lineshape, however, is indicative of only about 50% of the $>$50 porous Si nanoparticles studied. The remaining nanoparticles

exhibit much more interesting emission spectra with narrow lines and resolved fine structure as illustrated by the spectra in Figs. 4(B) and 4(C). The spectrum of Fig. 4(B) shows four resolved peaks and fits well to the sum of four Gaussians. Each Gaussian has a FWHM of approximately 115 meV, and the splitting between adjacent peaks is 160 meV (1300 cm^{-1}). The spectrum of Fig. 4(C) shows three resolved peaks and a splitting of 157 meV. Note the difference in the peak maximum ($\Delta\lambda_{max} \approx$ 75 nm) between the spectra of Figs. 4(B) and 4(C). We attribute the difference in λ_{max} to a difference
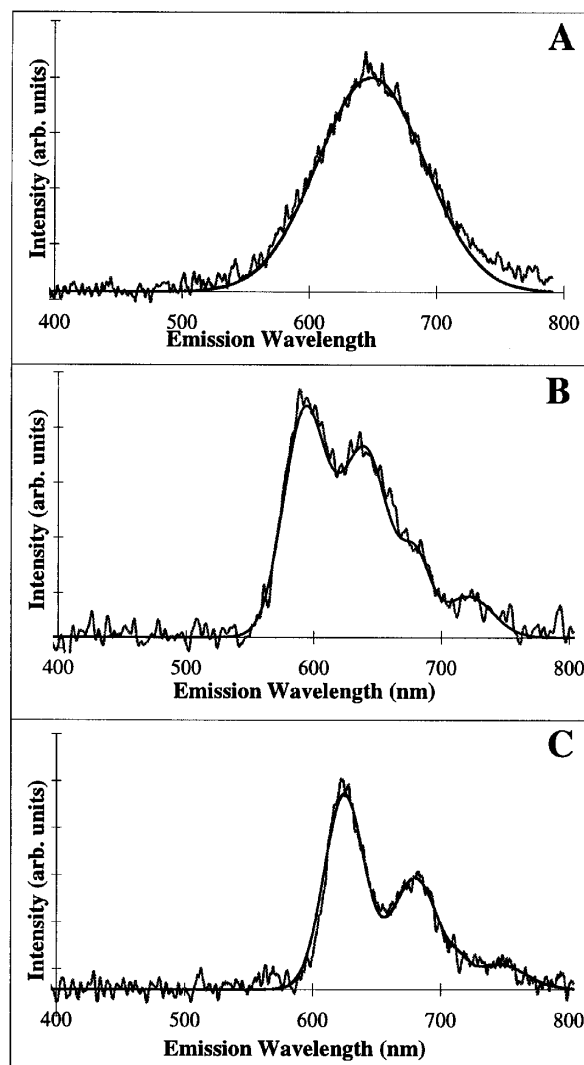

FIG. 4. Room temperature emission spectra of three porous Si samples. The smooth line represents a Gaussian fit (single or multiple) to each spectrum. Spectrum (A) is from a large ($>$500 nm) particle and was also fit to a single Gaussian. Spectrum (B) is from a $\sim$10 nm particle and was fit to the sum of four Gaussians. The 160 meV splitting is attributed to vibronic coupling to Si-O-Si groups on the surface of the quantum confined Si chromophore. Spectrum (C) is from a $\sim$10 nm particle and exhibits similar vibronic coupling (157 meV splitting). The difference in peak emission wavelength between spectra (B) and (C) is attributed to the difference in sizes of the chromophores as expected from the quantum size effect.

in the size of the chromophore (or chromophores) in each nanoparticle which is representative of the quantum size effect. It is important to note that we do not obtain an accurate size of the emitting species, only the size of the entire particle. We assume that each nanoparticle contains both the Si quantum dot (or dots) and oxide groups passivating the surface of the quantum dots. This implies that the size of the chromophore is much smaller than the size of the nanoparticle itself, and that the size of the emitting species in each nanoparticle is different. We also observe that the sum of the spectra from all of the nanoparticles studied converges to the spectrum observed for our bulk porous Si sample implying that the origin of the emission is similar for each.

The structure observed in the spectra in Figs. 4(B) and 4(C) is reminiscent of vibronic structure in molecular fluorescence. The size of the splitting, however, makes it unlikely that this fine structure is due to coupling to phonon modes in Si which are expected to be much smaller (around 55 meV) [4]. The only candidate in the appropriate frequency range for vibronic coupling are Si-O-Si stretching modes which have been observed in the $1100 - 1400$ cm^{-1} range in bulk porous Si [22]. Such modes exist in the surface passivating layer of the Si chromophore which we expect to contain oxide due to exposure of our samples to air.

The model for the luminescence of porous Si nanoparticles consistent with the results of our experiments is one in which the emission is mediated by the surface of the Si quantum dot. Excitons in the Si quantum dot are further confined near the surface of the quantum dot, and emission from these excitons is strongly coupled to vibrations in the surface passivating layer. This surface confinement also contributes to the blinking behavior by providing a means for nonradiative energy transfer. In addition, the observed blinking behavior and emission fine structure are indicative of emission from only a small number of emitting species. Thus, it is highly unlikely that emission from surface species such as siloxene (SiO_xH_y) could account for these phenomena due to the large number ($\gg 100$) of such species present on the surface of a 10 nm particle.

Our results also imply that controlled modification of the surface by species other than oxygen should produce dramatic differences in the emission yield, the blinking behavior, and the observed vibronic structure.

The characterization of these emission parameters from single nanoparticles with different surface terminating groups should provide important new insight into the role of the surface on the luminescence of porous Si and possibly lead to important breakthroughs in the application of porous Si in optical and optoelectronic devices. We are currently pursuing such experiments.

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