Dynamic Quenching of Porous Silicon Photoluminescence by Anthracene and 10-Methylphenothiazine

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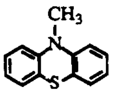
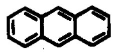
Canham's discovery of visible photoluminescence (PL) from porous silicon (po-Si) has created considerable research interest.[1] We have recently begun to explore the excited state properties of po-Si in the presence of known organic energy and electron transfer shuttles in nonaqueous solution.[2] The motivation behind these studies is to explore the possibility of using po-Si as a photocatalytic material potentially useful in solar energy conversion assemblies. More fundamentally, these studies may lead to a better understanding of the energetics, potential distribution, and carrier dynamics in these fascinating nanostructured materials.

In this communication, we report that the addition of anthracene (An) or 10-methylphenothiazine (MPTZ)



(MPTZ)



(An)

to a toluene solution leads to quenching of the po-Si PL intensity. Quenching of po-Si PL intensity by organic solvents,[3] amines,[4] metal salts,[5] and hydroxide ions[6] have been previously reported. However, this communication demonstrates, for the first time, that po-Si excited state(s) can be reversibly quenched by a dynamic mechanism.[7] Previously, only static quenching mechanisms have been invoked to rationalize the pH-dependent PL properties of po-Si.[6] The results and interpretation presented here suggest that carrier dynamics at this nanostructured interface can be tuned by molecular level modification.

Porous silicon samples were prepared by a technique which has been previously reported.[8] Briefly, p-type silicon wafers (boron doped, $\varrho = 1\ \Omega$ cm) were etched galvanostatically at a current density of 10 mA/cm^2 for 40 min in a 50 wt % HF solution. The samples were then washed with distilled water, glued to a glass rod with Ducco cement, fitted in a thermometer adapter, and clamped into a 14/20 ground glass joint inside a custom-built all-glass cell. The cell allows solutions to be changed without altering the po-Si sample geometry. Toluene was distilled over sodium or HPLC grade toluene (Fisher) was used as received, zone refined anthracene (Aldrich; 99+%) was used as received, and MPTZ (Pfaltz & Bauer) was recrystallized three times from toluene. PL measurements were performed with apparatus which has been previously described.[9]

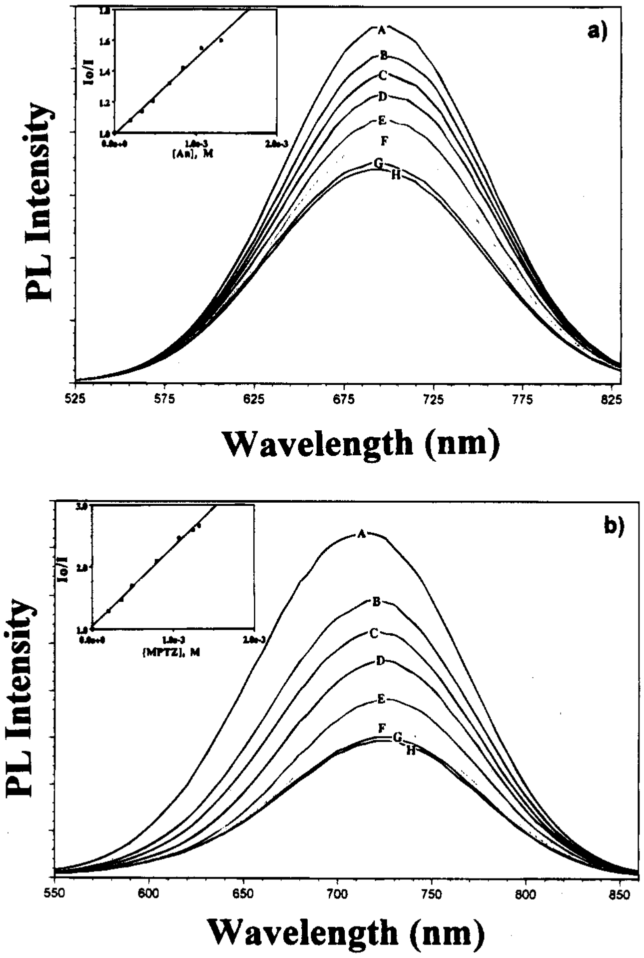


Figure 1. (a) PL spectra of a po-Si sample as a function of anthracene (An) concentration in toluene. The millimolar concentrations are (A) = 0.00; (B) = 0.19; (C) = 0.34; (D) = 0.47; (E) = 0.68; (F) = 0.84; (G) = 1.07; (H) = 1.31. (b) PL spectra of a po-Si sample as a function of 10-methylphenothiazine (MPTZ) concentration in toluene. The molar concentrations are (A) = 0.000; (B) = 0.20; (C) = 0.36; (D) = 0.49; (E) = 0.80; (F) = 1.07; (G) = 1.25; (H) = 1.32. The insets display Stern−Volmer plots of this same data. The excitation wavelength was 475 ± 4 nm and all data was recorded at room temperature.

The corrected photoluminescence spectrum of electrochemically etched porous silicon in toluene with and without An and MPTZ are shown in Figure 1a and 1b, respectively. For 10 representative samples, the PL maximum is observed at 710 ± 20 nm and the full width at half maximum is 2500 ± 200 cm^{-1}. Addition of An or MPTZ in toluene results in concentration dependent quenching of the PL intensity which can be restored to within 10% of the initial value by changing the solution back to neat toluene. Within experimental error, there is no change in the emission spectral distribution as a

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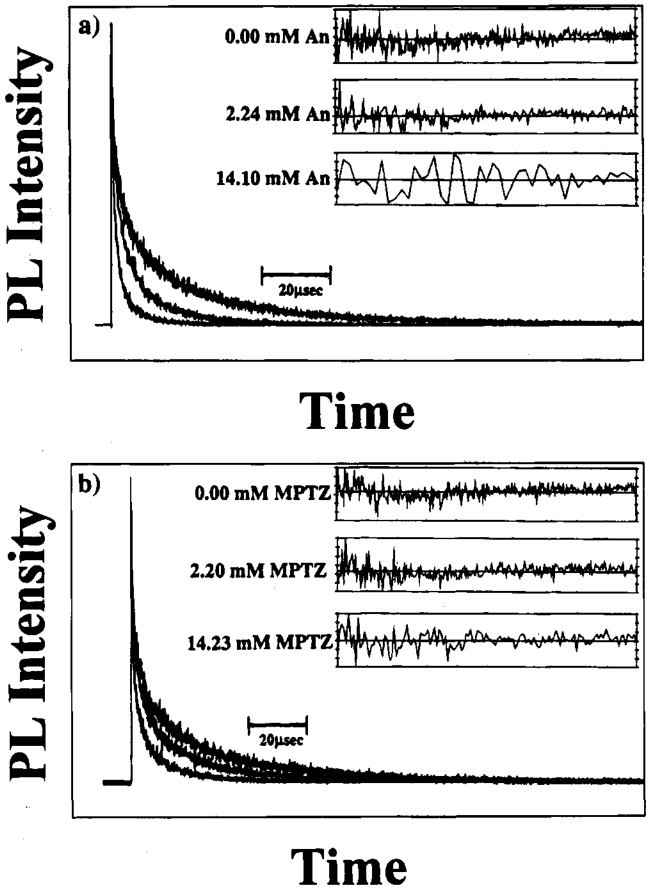

Figure 2. (a) Time-resolved photoluminescence decays of po-Si sample in toluene as a function of anthracene (An) concentration. The upper decay was obtained in neat toluene, the middle in 2.24 mM, and the bottom in 14.10 mM anthracene. (b) Time-resolved photoluminescence decays as a function of 10-CH_3-phenothiazine (MPTZ) concentration. The upper decay was obtained in neat toluene, the middle in 2.20 mM, and the bottom in 14.23 mM 10-methylphenothiazine. Residuals from fits to the Kohlrausch–Williams–Watts model (eq 1) are shown in the upper right-hand corners. Note that the 20 μs time scale corresponds only to the photoluminescence decays and not the residuals. The sample was excited with 460 nm light (40 μJ/pulse), and the photoluminescence was monitored at 710 ± 5 nm. The data presented are an average of 100 laser pulses.

function of acceptor concentration. Neither An or MPTZ absorb significantly at wavelengths longer than 400 nm, so the PL intensity decrease is not due to competitive absorption of the exciting or emitted light.

Time resolved PL decays of po-Si in toluene with and without quenchers is given in Figure 2. The kinetics are complex but can be well described by the Kohlrausch–Williams–Watts (KWW) model[10,11] (eq 1) as has

$$I(t) = \alpha \exp(-t/\tau)^{\beta} \tag{I}$$

been previously reported.[6,13] Residuals are shown as insets in Figure 2 to demonstrate the goodness of fit. In the KWW model the parameter β can be related to the width of an underlying continuous distribution of relaxation rates and τ is the lifetime at the maximum amplitude of the distribution.[11] A mean lifetime can be calculated by eq 2, where Γ represents the gamma

$$\langle\tau\rangle = (\tau/\beta)\Gamma(1/\beta) \tag{II}$$

function.[12] Mean lifetimes calculated from eq 2 were somewhat sample dependent, and values of 10 ± 5 μs were calculated for 10 representative porous silicon samples in toluene. In all cases, the addition of An or MPTZ results in a dramatically shortened, concentration dependent mean lifetime (Table 1). The parameter β is largely independent of solution concentration, which suggests that the distribution width is unperturbed by An and MPTZ exposure. The initial mean lifetime can be restored to within 5% of the initial value by replacing the solution mixture with neat toluene.

Table 1. Kohlrausch–William–Watts Analysis of po-Si Photoluminescence Decays in Toluene Solutions[a]

quencher concn (mM)[b]	τ (μs)	β	$\langle\tau\rangle$ (μs)[c]
0.00	2.39 ± 0.04	0.42 ± 0.01	7.22 ± 0.04
2.20 MPTZ	1.49 ± 0.06	0.43 ± 0.01	4.14 ± 0.04
6.31 MPTZ	0.888 ± 0.016	0.42 ± 0.01	2.66 ± 0.02
14.23 MPTZ	0.653 ± 0.049	0.43 ± 0.01	1.76 ± 0.06
2.24 An	1.01 ± 0.08	0.45 ± 0.01	2.49 ± 0.06
6.26 An	0.723 ± 0.029	0.48 ± 0.01	1.59 ± 0.02
14.10 An	0.243 ± 0.006	0.41 ± 0.01	0.738 ± 0.01

[a] The Kohlrausch–Williams–Watts model is given in eq 1. [b] Quencher concentration in toluene solution where An represents anthracene and MPTZ represents 10-methylphenothiazine. [c] Mean lifetime of po-Si in toluene solution; calculated using eq 2.

Interestingly, the PL data is well fit to the Stern–Volmer model (eq 3),[7] where I_0 and I represent the PL

$$I_0/I = 1 + K_{SV}[Q] \tag{III}$$

intensity in the absence and presence of quencher Q, respectively, and K_{SV} is the Stern–Volmer constant. Plots of I_0/I versus concentration are linear, and K_{SV} is typically $(1.0 \pm 0.5) \times 10^3$ M^{-1} for An and MPTZ. The sample-to-sample variation is sufficiently large that we cannot distinguish whether An or MPTZ is the better quencher. In all samples examined, however, good fits to the Stern–Volmer model were obtained by linear regression. Plots of $\langle\tau_0\rangle/\langle\tau\rangle$ versus quencher concentration are also linear, but the slopes are somewhat smaller than those obtained from steady state measurements. However, it is well-known that po-Si decay kinetics are dependent on the observation wavelength[6,13] and the quenching data may also depend on the excitation energy. Furthermore, it remains unclear whether mean lifetimes calculated using eq 2 have any real physical significance. Therefore, a more quantitative analysis of the lifetime data would be highly speculative at this time.

Whether quenching involves energy transfer, electron transfer, or some other less well-defined process remains unknown. Electron transfer from An ($E°(An^{0/+}) = +1.3$ V vs SCE)[14] and MPTZ ($E°(MPTZ^{0/+}) = +0.64$ V vs

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SCE)[15] to po-Si* is likely if the po-Si valence band edge is more positive. In addition, energy transfer from po-Si* to the triplet level of anthracene, ^{3}An = 1.8 eV, is thermodynamically feasible.[16] It has been shown previously that the PL intensity of po-Si is quenched by a variety of bases and can be restored by acid exposure, suggesting that surface acid–base chemistry is an important factor.[4,6] The lack of obvious basic character for the organic compounds studied here and the high degree of reversibility in nonaqueous solvent strongly suggest that Brønsted acid–base chemistry is not responsible for the dramatic PL changes.

In summary, these studies clearly reveal that excited state carrier dynamics of po-Si can be modified by An and MPTZ in toluene. For applications of po-Si as fast optical switches, the shortened excited state lifetime(s) in the presence of An and MPTZ is beneficial. An important goal for the development of high-bandwidth po-Si optical devices is the preparation of materials which are highly emissive and have a short excited-state lifetime. The results presented here suggest that molecular level modification may allow po-Si materials with increased bandwidth to be prepared, albeit at the expense of some photoluminescence intensity.

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