Room-temperature microparticle-based persistent spectral hole burning memory

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We show both theoretically and experimentally that a random distribution of spherical microparticles may be used as a spectral hole burning memory. This microparticle hole burning memory, which can be both written and read at room temperature, is a direct consequence of the properties of morphology-dependent resonances of microparticles. The narrow electromagnetic morphologically dependent resonances (MDR's) that are so distinctly present in single-particle experiments are virtually washed out in experiments on polydispersed distributions of particles. This is the case even for the narrowly distributed particles produced in space, space beads. In this Letter we present a means for encoding information into such a distribution of particles that takes direct advantage of the narrow MDR's. This procedure, known as microparticle hole burning, is to our knowledge the first example of the use of a collection of microparticles as a medium for persistent spectral hole burning. Unlike all other condensed-matter hole burning media, the microparticle hole burning medium does not have to be either written or read at cryogenic temperature; it operates at room temperature.

The principle of the microparticle hole burning memory is based on the fact that a given MDR occurs at a wavelength in proportion to the particle's size (with the refractive index held constant). Thus a collection of particles having a distribution of sizes gives rise to a photophysical response that is heterogeneous. A good example of this effect, as we show below, occurs for the case of the fluorescence excitation spectrum taken on an ensemble of dyed microspheres. Such a spectrum is composed of the sum of spectra from individual particles, each with resonances that occur at different wavelengths. Thus the normal homogeneously broadened excitation spectrum of a typical dye at room temperature is found to be inhomogeneous for measurements on an ensemble of dyed particles. Memory may be imprinted by a laser, for example, by preferentially photolyzing molecules within particles that have an MDR at resonance with the laser wavelength. The memory may be read out by taking the fluorescence excitation spectrum; photolysis causes fluorescence to be reduced, thus putting holes into the excitation spectrum. In what follows we review important aspects of MDR's, construct a simple model for understanding microparticle hole burning, and present results of experiments that confirm our basic idea.

A spherical particle of radius \(a\) irradiated by a plane wave of wavelength \(\lambda\) exhibits an enhanced internal field when its optical size \(X\) (circumference-to-incident-wavelength ratio, \(X = 2\pi a/\lambda\)) corresponds to a resonant condition. These resonances are distinguished by their polarization \(P\) (i.e., TE or TM), angular momentum \(l\), and radial order number \(s\) (i.e., the number of nodes of the wave function inside the particle). A general mode is labeled \(P_{l,s}\). The free spectral range in \(X\) between \(P_{l,s}\) and \(P_{l+1,s}\) is dependent chiefly on the refractive index, and consequently the wavelength difference between \(P_{l,s}\) and \(P_{l+1,s}\), \(\Delta\lambda\), is inversely proportional to \(X\) and proportional to \(\lambda\), i.e., the larger the particle size, the closer the spacing in wavelength near a given wavelength.

In Fig. 1 we show a simulated normal random distribution\(^5\) of \(10^4\) polystyrene particles having a mean radius \(\langle a\rangle\) of 1.44 \(\mu m\) and a ratio of standard deviation to average size \(\sigma_a/\langle a\rangle\) of 0.01. The arrows indicate the sizes of particles within the distribution that have MDR's in resonance at 588.3 nm. Our goal is to model

\[\text{Fig. 1. Simulated normal random distribution of } 10^4 \text{ polystyrene particles having a mean radius of } 1.44 \mu m \text{ and a standard deviation of } 1\% \text{ in this size. The arrows indicate the parts of the distribution in resonance with a laser at 588.3 nm.}\]
the fluorescence excitation spectrum of this ensemble. Since fluorescence is incoherent, an excitation spectrum for the distribution in Fig. 1 may be constructed by adding the Mie absorption of each of the particles. The curve in Fig. 2(a) is the Mie absorption of a single particle at the center of the distribution (\( \langle a \rangle = 1.44 \mu m \)) using a refractive index of 1.59 + 10^{-6}. The resonant features are clear. As the size of the particle changes, the resonances shift in accordance with our discussion above. The sum of the absorption from all 10^6 particles in Fig. 1 is shown in Fig. 2(b). We see that the collective fluorescence [Fig. 2(b)] has lost virtually all of the detail present in the single-particle spectrum. Now we suppose that an intense laser is projected onto the distribution at a wavelength \( \lambda_w \) of 588.3 nm. Although the rate of photolysis is expected to vary spatially owing to nonuniform absorption, for simplicity we assume that this rate is proportional to the power absorbed by the entire particle. As a consequence the fluorescence will fall exponentially with exposure time. With this recipe the initial fluorescence from each particle of size \( a \) is multiplied by \( F(a) = \exp[-\beta G(a)] \), with \( G(a) = a^2 Q_a(2\pi a/\lambda_w)/(\langle a \rangle)^2 Q_\infty(2\pi \langle a \rangle/\lambda_w) \), where \( Q_a(X) \) is the Mie absorption efficiency at optical size \( X \) and \( \beta \) is a parameter that is proportional the incident intensity of the photolyzing light, the quantum efficiency for photolysis and time. Figure 3 shows the fluorescence excitation spectra before \( (\beta = 0) \) and after \( (\beta = 1 \) or 20) the simulated photolysis. As one can plainly see, narrow holes are predicted that are clearly distinct from the noise due to number fluctuations. It should be noted that these holes become broadened beyond the width of the TEM_{01} resonance as \( \beta \) increases.

Although all three sizes indicated in Fig. 1 contribute to the hole at the write wavelength \( \lambda_w \) (i.e., 588.3 nm), the feature at 598 nm in Fig. 3 is principally contributed to by particles near the center of the distribution, \( a = 1.44 \mu m \). The fluorescence of these particles is bleached by stimulating their TEM_{01} resonance. Once bleached the particles will not fluoresce when probed at any of their other resonances. The feature at 598 nm in Fig. 3 is due in fact to the TM_{19} resonance of particles near 1.44 \mu m. Such a feature will be termed subsidiary since it owes its existence to only one of the three groups of particles. In this respect it is interesting to note that the model predicts that such subsidiaries become less distinct as the distribution becomes broader and contains more resonance that can be stimulated by the write wavelength (e.g., a distribution such that \( \sigma_w/(\langle a \rangle > \Delta \lambda/\lambda) \). All particles in resonances at \( \lambda_w \) contribute to the hole at this wavelength; however, other resonances (i.e., the subsidiary resonances) of these particles are separated from \( \lambda_w \) by an amount that depends distinctly on their individual sizes. Consequently the subsidiary resonances from different particles in the ensemble will not be in register; these subsidiaries become muted in comparison to the hole at \( \lambda_w \). In the experiments that follow we have chosen just such a distribution.

Our experiments were performed on dyed latex particles (\( \langle a \rangle = 12.1 \mu m, \sigma_w = 2.2 \mu m \)) on a cover glass slide. Latex particles dried from a hydrosol were dyed with Nile Red by stirring and sonicating the particles in a 10^{-4} M xylene solution. After centrifugation and decanting, a 1% Triton-X solution was added to the test tube containing the particles. After further stirring, centrifugation, and decanting, water was added. The contents of the test tube were then agitated by stirring and sonicating. This resulted in a resuspension of the now-dyed hydrosol particles. A drop of this dyed particle was placed on a cover glass slide. After air drying, this slide was placed on the stage of a fluorescence microscope and irradiated from above by a cw dye laser beam at 80° from the vertical. Fluorescence was isolated by filters (Corning CS 2-59 and CS 2-60) and detected by a cooled photomultiplier. The fluorescence from approximately 2000 particles in an area of 1 mm^2 was viewed by this detector.

Figure 4(a) shows the fluorescence excitation spectrum recorded on the sample at an incident intensity of 0.4 mW/cm^2 over a period of 10 min. After this scan the sample was irradiated for 11 min at 40 W/cm^2 with the wavelength fixed at 572.3 nm. Figure 4(b) shows the resulting excitation spectrum taken under the same conditions as in Fig. 4(a). The overall reduction in luminescence of the scan in Fig. 4(b) in comparison

![Fig. 2. (a) Simulated fluorescence excitation spectrum for a particle at the center of the distribution, \( a = 1.44 \mu m \). (b) Simulated fluorescence excitation spectrum for the particle distribution in Fig. 1.](image)

![Fig. 3. Fluorescence excitation spectra before (\( \beta = 0 \)) and after two simulated burns (\( \beta = 1 \) and 20) on the particle distribution in Fig. 1.](image)
with that of Fig. 4(a) is due to photolysis of the Nile Red dye. The hole in the spectrum in Fig. 4(b) at 572.3 nm is apparent. The lack of an apparent subsidiary hole is consistent with our model. The breadth of the hole is considerably wider than the width of a narrow resonance for particles of this size. However, this effect is similar to the effect that occurs in the model distribution for large $\beta$.

Although our model discloses the basic idea behind MHB, there are many theoretical questions to be answered in connection with this new memory system. How does one include the effects of the substrate? What is the effect of the proximity of one particle to another (i.e., many particles touch in our experiments)? (3) What is the consequence of a radial dependence in the distribution of dye within the particles? With respect to the first question, our own measurements and the measurements of others indicate that resonances remain intact on a glass surface. The second question is much harder to answer; however, recent calculations on light scattering from bispheres suggest an alteration in spectra for two identical particles in contact. However, even in this extreme case resonances are still predicted.

MHB may have interesting applications not only as a memory device but also in the diagnostics of particle size distributions. As we have pointed out, the degree to which subsidiary features are present is controlled by the ratio of $\sigma_d/\sigma$ to $\Delta \lambda/\lambda$.

Both theoretical questions and the possible use of MHB as a tool for evaluating size distributions are currently under study in our laboratories.

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References