Two-photon-induced three-dimensional optical data storage in CdS quantum-dot doped photopolymer

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The authors demonstrate three-dimensional erasable bit optical data storage in a quantum-dot doped photopolymer under two-photon excitation by a near-infrared femtosecond pulsed laser beam. It is shown that the photorefractive polymer consisting of poly(vinyl carbazole), ethyl carbazole, 4-(diethylaminobenzylidene)-malononitrile, and CdS quantum dots exhibits the changes not only in refractive index but also in fluorescence. Such a photosensitivity provides a multimode readout mechanism. In particular, the use of S rich surface quantum dots not only allows the two-photon-induced bit optical data storage with greater contrast but also expands the margin between permanent and erasable recording thresholds. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2724902]

The need for ever increasing amounts of data storage capacity compels the use of three-dimensional (3D) optically based systems. One of the promising methods for 3D optical data storage is based on volume holography.[1,2] In this regard, photorefractivity storing information in a change in refractive index has been identified as an erasable mechanism.[1,2] In particular, the use of the photorefractivity in polymers has resulted in low cost and efficient volume holographic recording media.[1,3] Semiconductor nanocrystals exhibit attractive optical properties such as narrow emission bands, emission wavelength tunability with size, and photostability.[4] Recently, the volume holographic data storage performance has been further enhanced by incorporating semiconductor nanocrystals such as CdS and CdSe quantum dots (QDs) in photorefractive polymers.[5,6]

Two-photon (2P) bit by bit memory is, on the other hand, another promising 3D optical data storage system which gives rise to a higher storage density than single-photon excitation.[7] 2P-induced multilayer optical recording has been successfully demonstrated in various erasable and nonerasable materials,[8–11] in particular, including photorefractive materials.[12,13] Although it has been shown that 2P excitation is applicable in a densely packed nonerasable QD film,[14] no 2P-induced 3D recording in QD-doped photorefractive polymers has been demonstrated. In this letter, for the first time, to our best knowledge, we report on 2P-induced erasable multimode 3D bit optical data storage in a CdS QD-doped photorefractive polymer.

It has been well known that the surface states of QDs significantly affect their photorefractive performance.[6,15] Thus, in our experiment, CdS QDs with different surface stoichiometries ranging from Cd rich to S rich were prepared. CdS core particles of 4.6 nm in diameter were prepared with a well established recipe.[16] Tuning the surface stoichiometry of CdS QDs from Cd rich to S rich was achieved in a one-pot method by systematically injecting controlled amounts of additional S precursors.[17] The only passivating ligand available in the system is oleic acid, which is expected to bind solely to surface Cd atoms, leaving any surface S atoms unpassivated. The Cd rich, mixed, and S rich surfaces were achieved at the mole concentration ratio of Cd to S of 1.2:1, 1:1.25, and 1:1.5, respectively. Both the absorption and photoluminescence (PL) spectra of surface processed QDs were measured immediately after they were taken from the reaction pot without any washing process to change the surface. Figure 1(a) shows the absorption spectra of as-prepared QDs, exhibiting a slight redshift of the first absorption peak due to the growth of the particle size with the adhesion of S. Figure 1(b) depicts a systematic reduction of PL when the surface density of S atoms of unpassivated dangling bonds was increased. Such a relative reduction of

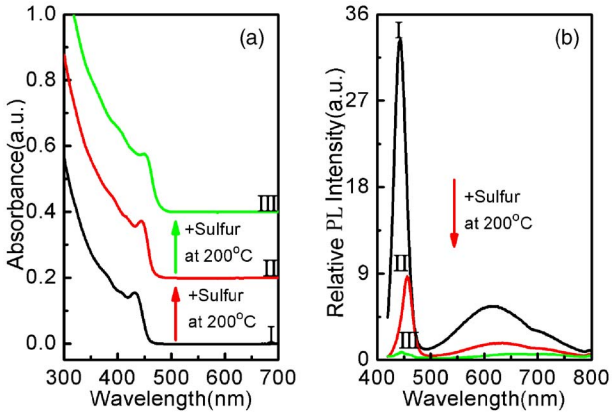

FIG. 1. (Color online) (a) Absorption and (b) relative PL spectra of the prepared QDs. I, II, and III correspond to QDs of the Cd rich, mixed, and S rich surfaces, respectively.

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the PL implies the photoinduced charge transfer and trapping in the surface of the QDs as S atoms serve as hole traps on the order of picoseconds,[18] which is the physical basis for 2P recording reported in this letter.

To investigate the recording performance of the surface processed CdS QDs under 2P excitation, we prepared a typical photorefractive polymer formulation consisting of poly(vinyl carbazole) (PVK), ethyl carbazole (ECZ), and 4-(diethylaminobenzylidene)-malononitrile (DABM).[19] The QD-based photorefractive polymer was prepared as follows.[5] 1 ml aliquots of raw QDs were taken from the reaction pot, washed, and precipitated by chloroform and 2-propanol. The precipitated particles were redissolved in chloroform and stored in the dark. The mixture of 54 mg of PVK, 16 mg of ECZ, 30 mg of DABM, and 0.12 nmol QDs were dissolved in chloroform. The solution was drop casted to a glass slide and dried at 60 °C for 20 min. The sample was heated to 150 °C for 3 min and subsequently sandwiched with a Teflon spacer of a thickness 20 μm.

The optical recording system for 2P excitation in the CdS-doped polymer is similar to that published elsewhere.[13] Since the samples have no linear absorption beyond the wavelength of 600 nm, a Ti:sapphire ultrashort pulsed laser beam of pulse width 100 fs (Spectra-Physics Tsunami) at a wavelength of 780 nm was employed as a light source for 2P excitation. An objective [numerical aperture (NA)=0.7; 20×] was used to focus the beam onto the recording media. In this case, there were over 300 QDs in the focal volume.[20] The exposure time for each bit is 30 ms. The 2P-induced data storage performance in the photorefractive polymer doped with the surface processed CdS QDs is illustrated in Figs. 2(a)–2(c).

Figure 2(a) shows the fluorescence readout images of bits recorded with different power levels. Each image comprises a pattern of 3×3 bits and a bit spacing of 10 μm. The fluorescence was excited by the ultrafast laser of wavelength 780 nm and power 4 mW and collected by a photomultiplier tube at the wavelength of 550 nm, which corresponds to the emission band of DABM. It is noted that the fluorescence intensity is substantially depressed upon radiation where QDs were present. Furthermore, the fluorescence quenching effect can be significantly enhanced for a given exposure power level [see Fig. 3(a)] as the surface of the QDs was engineered from Cd rich to S rich.

This fluorescence quenching effect may be physically explained as follows. Upon 2P excitation in recording, a space charge separation is established in the illuminated region, as suggested by the suppression of PL shown in Fig. 1(b). In the reading process, both QDs and DABM molecules are excited. In the region illuminated in the recording process, the local electric field caused by the charge separation at the surface of QDs and pointed to the center of QDs promotes the transfer of the excited electrons in DABM molecules to QDs,[15] thus reducing the fluorescence emission strength.

Another effect of the local electrical field is the possible nonlinear response such as the electro-optic effect and the alignment of DABM molecules. As a consequence, a change in refractive index in the focal region becomes possible. This refractive index change can be confirmed by transmission readout as well as differential interference contrast (DIC) readout, as shown in Figs. 2(b) and 2(c), respectively. All images were taken in a commercial microscope (Olympus BX50) with a high NA objective (NA=1.4). In the presence of QDs, there was a substantial increase in the readout contrast. The tendency became prominent when we gradually increased the hole-trap density by tuning the QD surface from Cd rich to S rich [Figs. 3(b) and 3(c)].

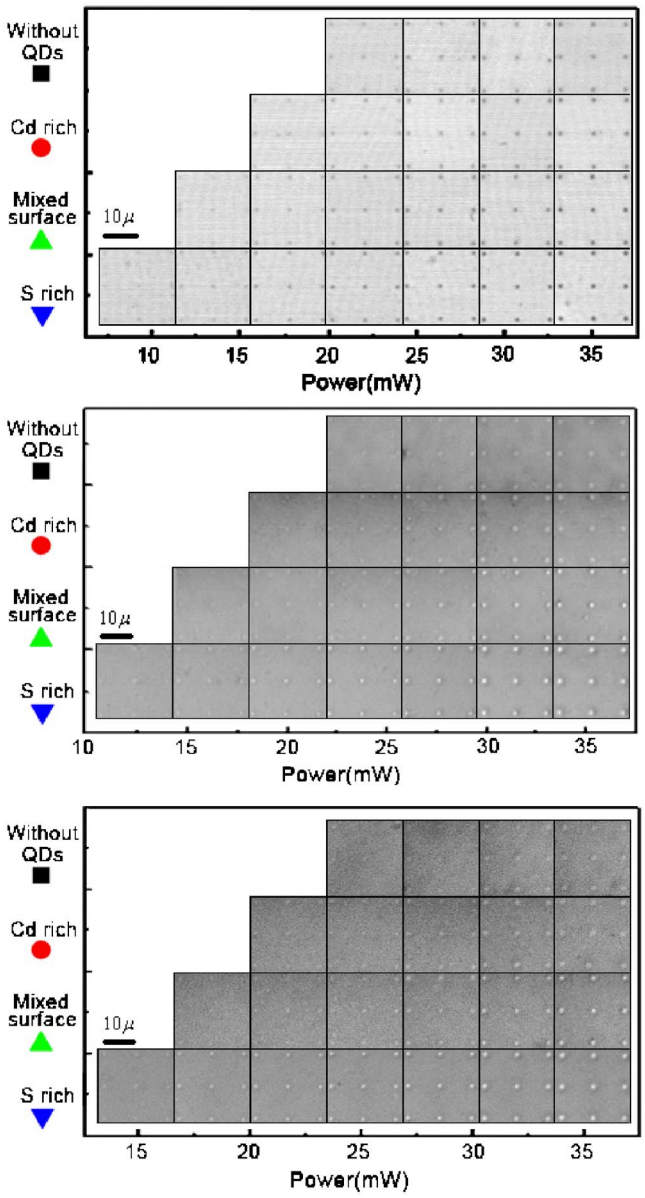

FIG. 2. (Color online) (a) Fluorescence, (b) transmission, and (c) DIC readout images of recorded bits in four different samples. The black squares, red dots, green triangles, and blue triangles correspond to samples without QDs and with CdS QDs of Cd rich surfaces, mixed surfaces, and S rich surfaces, respectively. The scale bar is 10 μm.

The threshold of the recording power decreases monotonically upon the appearance of QDs [see Fig. 3(d)]. In particular, in the presence of CdS QDs with S rich surfaces, the threshold power drops nearly 30% compared with the sample without QDs. Interestingly, the recorded bits below the threshold of the permanent recording power can be erased completely after exposure to an UV beam for 5 min. The margin between the threshold of erasable and permanent recording powers is enlarged as the transition of the QD surface progresses from Cd rich to S rich. After incorporating CdS QDs with a S rich surface, the rewritable recording range of the sample is more than 200% that of the sample without QDs.

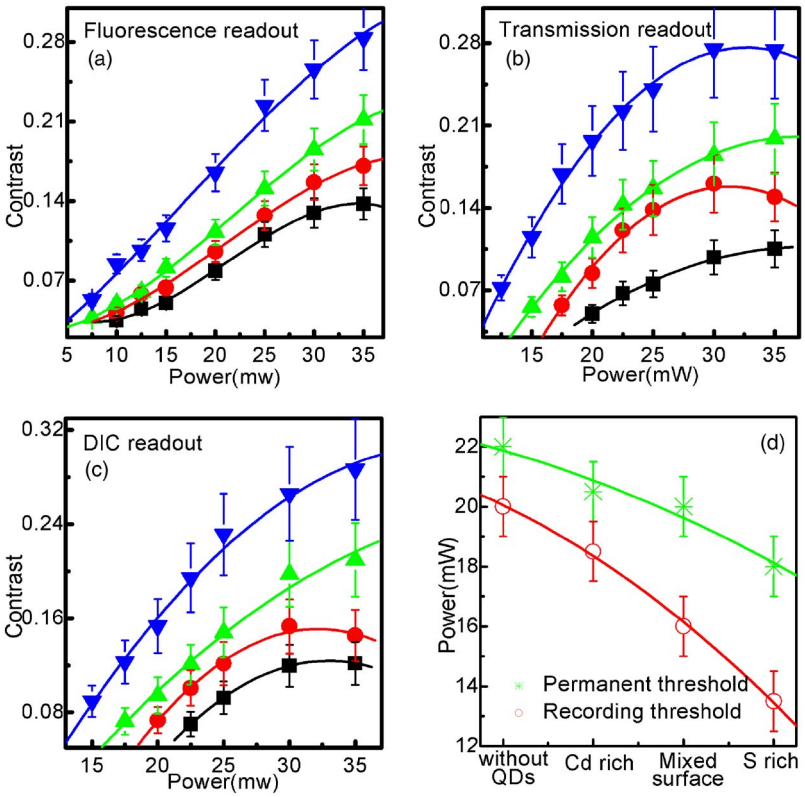

FIG. 3. (Color online) Multimode readout of recorded bits with (a) PL, (b) transmission, and (c) DIC readout contrasts as a function of the recording power in the four samples. (d) shows the recording threshold power (red circle) and permanent recording threshold power (green asterisk) as a function of surface modification.

Finally, to demonstrate the 3D optical data storage performance according to the principle revealed in Figs. 2 and 3, we show that multilayered information can be distinctly recorded and retrieved in the sample. In Figs. 4(a)–4(c), three layers of information were stored in the volume of the sample doped with the CdS QDs of a S rich surface. Each layer contains a pattern of 24×24 bits with a bit spacing of 3.2 μm. Letters A, B, and C were recorded in the first, second, and third layers, respectively, with a layer spacing of 20 μm, which leads to a storage density of approximately 5 Gbits.

In conclusion, we have demonstrated that the 2P excitation in the focus spot of an objective can be applied to introduce fluorescence quenching as well as refractive index change in a QD-doped photorefractive polymer. Consequently, multilayered 3D erasable bit optical data storage can be achieved. Engineering the surface of the CdS QDs from Cd rich to S rich leads to an expansion of the margin between the permanent and erasable recording thresholds by a factor of 2.

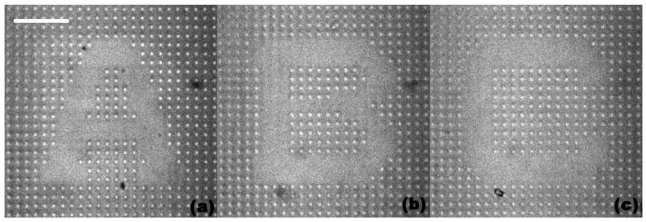

FIG. 4. (a) Letter A recorded in the first layer, (b) letter B recorded in the second layer, and (c) letter C recorded in the third layer. The scale bar is 20 μm.

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