

Very High Third-Order Nonlinear Optical Activities of Intrazeolite PbS Quantum Dots

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Semiconductor quantum dots (QDs) dispersed in glass and polymer matrixes have shown third-order nonlinear optical (3NLO) properties^{1–12} which can be exploited for fabrication of optical switches, waveguides, optical limiters, and many others. However, their sensitivities have not yet reached to the degrees sufficient for practical applications.

Zeolites are excellent hosts for QDs^{13–21} and have many advantages over glass and polymers due to the following. The zeolite-encapsulated QDs are usually smaller than 1.5 nm; their sizes are highly uniform, and they exist very regularly within the crystalline hosts. Despite the above characteristics, the measurements of the 3NLO properties of zeolite-encapsulated QDs have not been made due to the difficulty of preparing zeolite films supported on optically transparent substrates, such as glass and quartz, with reasonably high binding strengths between the films and substrates. For instance, when zeolite-Y films are grown on ordinary glass or fused silica, they readily peel off the substrates during drying, ion exchange with other ions, and calcination to remove organic contaminants. Furthermore, the strong tendency of many QDs to be expelled from the zeolite pores to the external surfaces by moisture²¹ has also hampered the measurements.

We now report that zeolite-Y films grown on the surfaces of indium-tin-oxide-coated (ITO) glass plates remain firmly bonded to the substrates during ion exchange with Pb²⁺ ions, drying, and formation of PbS by treating Pb²⁺ ions with H₂S and that the encapsulated PbS QDs show very high 3NLO activities.

The zeolite-Y films (thickness = 2 μm) supported on ITO glass (denoted as Y_g, average size = ~2 × 2.5 cm²) were prepared according to the procedure described in SI-1. The surface-polished Y_gs (thickness = 1.5 μm) became transparent (SI-2). Several Y_gs loaded with different numbers (*n* = 0, 8, 14, 23, and 33) of PbS in a unit cell were prepared [denoted as (PbS)_{*n*}-Y_g] according to the procedure described in SI-3.

The intrazeolite PbS QDs slowly migrated from the interior to the external surfaces and formed 3–20 nm-sized PbS QDs on the external surfaces upon exposure of (PbS)_{*n*}-Y_g (*n* ≥ 8) to the atmosphere (SI-4). To prevent the above phenomenon, the surfaces of dry (PbS)_{*n*}-Y_g were coated with octadecyl groups using octadecyltrimethoxysilane (ODM) in a glove box charged with dry argon (SI-5). Analyses of Pb²⁺-exchanged Y, moisture-exposed (PbS)_{*n*}-encapsulating Y, and ODM-coated (PbS)_{*n*}-encapsulating Y crystals with transmission electron microscope (TEM) (SI-4), ²⁷Al and ²⁹Si NMR spectra (SI-6), and X-ray diffraction patterns (SI-7) revealed that the formation of PbS results in partial framework rupture, due to simultaneous incorporation of H⁺ during the process of PbS formation.¹⁷ Furthermore, the analyses revealed that ODM coating effectively prevents PbS QDs from leaving the internal

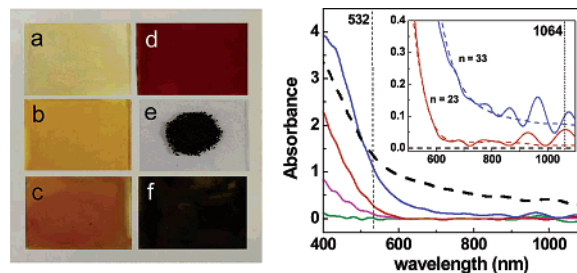


Figure 1. Left: The photographs of ODM-(PbS)_{*n*}-Y_g for 8 (a), 14 (b), 23 (c), and 33 (d), the bulk PbS powder on a Y_g plate (e), and moist (PbS)₃₃-Y_g (f). Right: Absorption spectra of ODM-(PbS)_{*n*}-Y_g for *n* = 8 (green), 14 (pink), 23 (red), and 33 (blue), and moist-(PbS)₃₃-Y_g (black dash). Inset: Enlarged spectra of *n* = 23 and 33 in the 500–1100 nm region. The dashed curves represent the corresponding estimated absorption spectra free from interference patterns.

Table 1. 3NLO Activities of (PbS)_{*n*}-Intercalating Zeolite-Y Films

ODM-(PbS) _{<i>n</i>} -Y _g	532 nm		1064 nm	
	γ ($\times 10^{-12}$ cm ² /W)	β (cm/GW)	γ ($\times 10^{-12}$ cm ² /W)	β (cm/GW)
8				
14	-11	85		
23	-34	290	-32	-72
33	-294 (-6) ^a	5900 (-50) ^a	-130 (-1) ^a	-1440 (46) ^a
33 (moist)		45		

^a Highest literature values (ref 7).

pores, as in other cases (SI-4).²¹ The ODM-coated and moisture-exposed (PbS)_{*n*}-Y_gs are denoted as ODM-(PbS)_{*n*}-Y_g and moist-(PbS)_{*n*}-Y_g, respectively.

The color of ODM-(PbS)_{*n*}-Y_g progressively red-shifted from pale yellow to deep red with increasing *n* (Figure 1, left, a–d). The colors were distinctively different from black, the color of bulk PbS (e). The color of moist-(PbS)₃₃-Y_g was black (f), consistent with the presence of large PbS QDs (3–20 nm) on the external surfaces. The absorption (Figure 1, right) spectra show that the amount of PbS QDs that absorb at 532 nm increases with increasing *n*. The enlarged spectra (inset) further revealed that the samples with *n* = 23 and 33 contain intrazeolite QDs that absorb even at 1064 nm, although very weakly (abs = 0.01 and 0.07, respectively). Moist-(PbS)₃₃-Y_g showed absorption over the entire visible region and even beyond 1100 nm (Figure 1, right, black dashed curve), due to large PbS QDs existing on the external surfaces (see SI-8 for the verification of QDs within zeolite and the nonexistence of excitonic bands in the spectra).

The nonlinear refraction (γ) and absorption (β) coefficients (SI-7) of the films at 532 and 1064 nm, respectively, are shown in Table 1. They were measured using the *z*-scan method (SI-9) using mode-locked picosecond laser pulses (pulse width = 50 ps) at two

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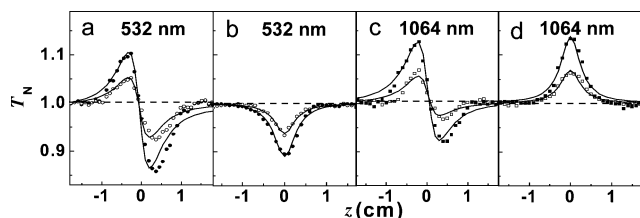


Figure 2. The z -scan data (symbols) and theoretically fitted curves (solid curves) of ODM-(PbS)₃₃-Y_g obtained under the closed (a) and open (b) aperture conditions at 532 nm and under the closed (c) and open (d) aperture conditions at 1064 nm. Input irradiances at the focal point were 0.10 and 0.18 GW/cm² at 532 nm and 0.27 and 0.47 GW/cm² at 1064 nm.

different pulse powers. Figure 2 represents the plots of the normalized transmittance (T_N) versus the propagation path (z) of a focused quasi-Gaussian beam of ODM-(PbS)₃₃-Y_g. The threshold pulse powers that start damaging the zeolite films were 5.23 (at 532 nm) and 2.51 (at 1064 nm) GW/cm², respectively.

The 3NLO activity of ODM-(PbS) _{n} -Y_g at 532 nm increased with increasing n , in correlation with the absorption intensity at the wavelength. The absence of activities from the samples with $n = 0$ and 8 shows that the 3NLO activity does not come from the bare zeolite film, ITO glass substrate, or surface-coated ODM. Similarly, the activity at 1064 nm increased in correlation with the absorption intensity of PbS QDs at the wavelength ($n \geq 23$). The above results unambiguously show that the active species are intrazeolite PbS QDs, and their 3NLO activities occur by resonant processes (the responses that are triggered by absorption of QD). The fact that moist-(PbS)₃₃-Y_g gave very weak 3NLO response shows that, while the intrazeolite PbS QDs are active, the large external PbS QDs are not or weakly active.

The obtained γ and β values of ODM-(PbS)₃₃-Y_g at 532 nm are larger by 47 and 118 times, respectively, in magnitude than the highest values ever measured from PbS QDs (-6 and -50 , respectively),⁷ and the values at 1064 nm are larger by 130 and 31 times, respectively, in magnitude than the highest values ever measured from PbS QDs (-1 and 46, respectively) under similar input pulse conditions.⁷ The values at 1064 nm are still larger by 23 and 18 times than the values observed from GaAs dispersed in vycor glass,⁵ which are the highest values ever observed from QDs.

The negative γ values reveal that the PbS QDs show a self-defocusing behavior at both wavelengths. The β values are positive (at 532 nm) and negative (at 1064 nm), indicating that the PbS QDs behave as strong excited-state absorbers and optical bleachers, respectively, at the corresponding wavelengths. Opposite signs of β were observed from larger PbS QDs dispersed in polyvinyl alcohol.⁷ The measured relaxation time of PbS QDs at 532 nm was less than 100 ps (SI-10), which is short enough for them to be applied for optical switching devices.

The 3NLO activities of PbS QDs in other media were also measured by others at various wavelengths with various pulse widths.^{8–12} Since the 3NLO activity varies with varying pulse width and wavelength of the laser beam, comparison of the figures of merit ($\chi^{(3)}/\alpha_0$ and γ/α_0 , where $\chi^{(3)} = 3\text{NLO susceptibility}$ and $\alpha_0 = \text{linear absorption coefficient}$) should be conducted when the data were obtained under similar measurement conditions. The $\chi^{(3)}/\alpha_0$ and γ/α_0 of ODM-(PbS)₃₃-Y_g were 3.4×10^{-12} esu $\cdot\text{cm}$ and -4×10^{-14} cm²/W $\cdot\text{cm}$ at 532 nm and 2.3×10^{-11} esu $\cdot\text{cm}$ and -2.8×10^{-13} cm²/W $\cdot\text{cm}$ at 1064 nm, respectively. When compared with the γ/α_0 value reliably obtained from 2.3 to 3.5 nm PbS QDs dispersed in silica–titania film (-5×10^{-15} cm²/W $\cdot\text{cm}$, see SI-11),¹¹ which was measured under similar conditions (60 ps pulse width at 1064 nm), the γ/α_0 value of ODM-(PbS)₃₃-Y_g is more than 56 times higher.

The fact that the 3NLO activities of ODM-(PbS) _{n} -Y_g occur by resonant processes indicates that the activities originate from the laser-induced transient changes in the absorption spectra.¹ The following are proposed to cause the very high 3NLO activities. The sizes of QDs (< 1.5 nm) are smaller than those that have been dispersed in other media (> 2.5 nm) due to encapsulation in zeolite pores. Second, zeolite pores can accommodate a large number of QDs without transforming them to larger QDs due to the rigidity of the pore systems. Third, the strong electric field within the pores greatly stabilizes the generated excitons, which also provides the opportunity to form even biexcitons, whose formation is favored with decreasing the QD size.²

This work thus reports for the first time that zeolite-encapsulated PbS QDs show very high 3NLO activities. Since there are many different types of QDs and many different types of zeolites with different pore sizes, pore shapes, pore networking, framework compositions, and cations, we expect that the development of 3NLO materials with much higher sensitivities operable at various wavelengths is just a matter of time. Thus, this work provides not only a promising new direction to which the search for highly sensitive 3NLO materials has to be conducted but also a new direction to which zeolite research and applications have to be expanded.

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Supporting Information Available: Experimental procedures, SEM and TEM images, solid-state NMR spectra, and X-ray diffraction pattern. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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