Semantic quantum dots (QDs) dispersed in glass and polymer matrices have shown third-order nonlinear optical (3NLO) properties\(^1\) 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\(^1^3\)–\(^2^1\) 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 ion exchange, 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 moisture\(^2^1\) 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 Pb\(^{2+}\) ions, drying, and formation of PbS by treating Pb\(^{2+}\) ions with H\(_2\)S and that the encapsulated PbS QDs show very high 3NLO activities.

The zeolite-Y films (thickness = 2 \(\mu\)m) supported on ITO glass (denoted as \(Y_g\), average size = 2 \(\times\) 2.5 \(\mu\)m) were prepared according to the procedure described in SI-1. The surface-polished \(Y_g\)s (thickness = 1.5 \(\mu\)m) became transparent (SI-2). Several \(Y_g\)s loaded with different numbers (\(n = 0, 8, 14, 23, 33\)) 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 upon exposure of (PbS)\(_n\)-\(Y_g\)s to the atmosphere (SI-4). To prevent the above phenomenon, the surfaces of dry (PbS)\(_n\)-\(Y_g\)s were coated with octadecyl groups using octa-decyltrimethoxysilane (ODM) in a glove box charged with dry argon (SI-5). Analyses of Pb\(^{2+}\)-exchanged \(Y_g\), moisture-exposed (PbS)\(_n\)-encapsulating \(Y_g\), and ODM-coated (PbS)\(_n\)-encapsulating \(Y_g\) crystals with transmission electron microscope (TEM) (SI-4), \(^{27}\)Al and \(^{29}\)Si 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.\(^2^7\) Furthermore, the analyses revealed that ODM coating effectively prevents PbS QDs from leaving the internal coats, as in other cases (SI-4).\(^2^1\) The ODM-coated and moisture-exposed (PbS)\(_n\)-\(Y_g\)s are denoted as ODM-(PbS)\(_n\)-\(Y_g\), and moist-(PbS)\(_n\)-\(Y_g\), respectively.

The color of ODM-(PbS)\(_n\)-\(Y_g\)s 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 (\(\gamma\)) and absorption (\(\beta\)) 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

\[\begin{array}{ccc|cc|cc}
 n & 532 nm & 1064 nm \\
 \hline
 8 & \gamma & 10^{-12} \text{cm}^2/\text{W} & \beta & \text{cm/GW} \\
 14 & -11 & 85 & -32 & 72 \\
 23 & -34 & 290 & -130 (-1)^a & -1440 (46)^a \\
 33 (moist) & -294 (-6)^a & 5900 (-50)^a & 45 \\
\end{array}\]

\(^a\) Highest literature values (ref 7).

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Figure 1. Left: The photographs of ODM-(PbS)\(_n\)-\(Y_g\) for \(n = 8\) (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

<table>
<thead>
<tr>
<th>ODM-(PbS)(_n)-Y(_g)</th>
<th>(n)</th>
<th>532 nm</th>
<th>1064 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma) (cm(^3)/GW)</td>
<td>(\beta) (cm/GW)</td>
<td>(\gamma) (cm(^3)/GW)</td>
<td>(\beta) (cm/GW)</td>
</tr>
<tr>
<td>8</td>
<td>-11</td>
<td>85</td>
<td>-32</td>
</tr>
<tr>
<td>14</td>
<td>-34</td>
<td>290</td>
<td>-130 (-1)(^a)</td>
</tr>
<tr>
<td>23</td>
<td>-294 (-6)(^a)</td>
<td>5900 (-50)(^a)</td>
<td>45</td>
</tr>
<tr>
<td>33 (moist)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Highest literature values (ref 7).
different pulse powers. Figure 2 represents the plots of the normalized transmittance ($T_0$) versus the propagation path ($z$) of a focused quasi-Gaussian beam of ODM-(PbS)$_{33}$-$Y_6$. The threshold pulse powers that start damaging the zeolite films were 5.23 (at 532 nm) and 2.51 (at 1064 nm) GW/cm$^2$, respectively.

The 3NLO activity of ODM-(PbS)$_{33}$-$Y_6$ 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 intraframework PbS QDs, and their 3NLO activities occur by resonant processes (the responses that are triggered by absorption of QD). The fact that moist-(PbS)$_{33}$-$Y_6$ gave very weak 3NLO response shows that, while the intraframework PbS QDs are active, the large external PbS QDs are not or weakly active.

The obtained $\gamma$ and $\beta$ values of ODM-(PbS)$_{33}$-$Y_6$ at 532 nm are larger by 47 and 118 times, respectively, in magnitude than the highest values ever measured from PbS QDs ($\approx 6$ and $\approx 50$, respectively), 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 ($\approx 1$ and 46, respectively) under similar input pulse conditions. The values at 1064 nm are still larger by 23 and 18 times than the values observed from GaAs dispersed in vycor glass, which are the highest values ever observed from QDs.

The negative $\gamma$ values reveal that the PbS QDs show a self-defocusing behavior at both wavelengths. The $\beta$ 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 $\beta$ were observed from larger PbS QDs dispersed in polyvinyl alcohol. 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. 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 $\gamma/\alpha_0$, where $\chi^{(3)}$ is 3NLO susceptibility and $\alpha_0$ = linear absorption coefficient) should be conducted when the data were obtained under similar measurement conditions. The $\chi^{(3)}/\alpha_0$ and $\gamma/\alpha_0$ of ODM-(PbS)$_{33}$-$Y_6$ were $3.4 \times 10^{-12}$ esu·cm and $-4 \times 10^{-14}$ cm$^2$/W·cm at 532 nm and $2.3 \times 10^{-11}$ esu·cm and $-2.8 \times 10^{-13}$ cm$^2$/W·cm at 1064 nm, respectively. When compared with the $\gamma/\alpha_0$ value reliably obtained from 2.3 to 3.5 nm PbS QDs dispersed in silica–titania film ($\approx 5 \times 10^{-15}$ cm$^2$/W·cm, see SI-11) which was measured under similar conditions (60 ps pulse width at 1064 nm), the $\gamma/\alpha_0$ value of ODM-(PbS)$_{33}$-$Y_6$ is more than 56 times higher.

The fact that the 3NLO activities of ODM-(PbS)$_{33}$-$Y_6$ occur by resonant processes indicates that the activities originate from the laser-induced transient changes in the absorption spectra. 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.

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.

References

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