Increase of Third-Order Nonlinear Optical Activity of PbS Quantum Dots in Zeolite Y by Increasing Cation Size

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S *Supporting Information*

ABSTRACT: The third-order nonlinear optical (3NLO) activity of PbS quantum dots (QDs) encapsulated in zeolite Y has been expected to depend sensitively on the countercation of the zeolite host. However, ion exchange of the pristine countercation, H^+, with other cations has not been possible because the framework decomposes and the QDs aggregate immediately when the PbS QD-incorporating zeolite Y with H^+ as the countercation is exposed to the atmosphere. We now report that when H^+ is transformed to NH_4^+, the framework of PbS QD-containing zeolite Y does not undergo decomposition and the PbS QDs do not undergo aggregation to form larger QDs during the aqueous ion exchange of NH_4^+ with alkali-metal ions (M_A^+ = Li^+, Na^+, K^+, Rb^+). The 3NLO activity of the M_A^+-exchanged PbS QD-incorporating zeolite Y film increases with increasing size of M_A^+. The stabilization of the surface-bound exciton by the electron-rich framework oxide and electron-poor cation is proposed to be responsible for the increase. This is the first example of a method for systematically increasing the 3NLO activity of QDs dispersed in a dielectric matrix by systematically changing its properties. These results will serve as a guideline for future research and also promote applications of QD-incorporating zeolites in various fields.

In third-order nonlinear optical (3NLO) materials, the refractive index (n) and absorption coefficient (α) change reversibly with changes in the intensity of the incident beam (I) according to eq 1,

$$n = n_o + \gamma I \qquad \alpha = \alpha_o + \beta I \qquad (1)$$

where n_o and α_o are the refractive index and absorption coefficient in the low-I limit, respectively, and γ and β are the nonlinear refractive index and absorption coefficient, respectively. Because of these properties, 3NLO materials are used for optical switches,[1−3] waveguides,[4,5] optical limiters,[6] saturable absorbers,[7,8] and IR detectors for medical and military applications. Although various materials have been shown to possess 3NLO properties (section SI1 in the Supporting Information), the search for materials with exceptional 3NLO properties must be continued. Among possible candidates, semiconductor quantum dots (QDs) dispersed in dielectric matrices have received the most attention.[9−23] However, their 3NLO activities have not been high enough for practical use, so intense research in this field is still necessary.

There are two types of processes in 3NLO activity: resonant and nonresonant.[9] In a resonant process, the frequency of the incident beam overlaps with a one- or multiphoton electronic absorption band, and the transient change in α induced by light absorption gives rise to the 3NLO activity. The smallest possible semiconductor QDs with narrow size distributions and high extinction coefficients (e.g., PbS and GaAs) have been expected to give high 3NLO responses.[9] In a nonresonant process, the frequency of the incident beam does not overlap with an electronic absorption band. The 3NLO activity then occurs because of the interaction of the local field of the host−guest complex arising from the difference in the n values of the host and guest or from the dipole−dipole interaction between the host and guest materials and the oscillating electric field of the incident beam.[9] Semiconductor materials with larger sizes have been regarded to be more active because their n values and dipole moments increase with increasing size.

With the above background in mind, and from the well-established fact that zeolites are excellent hosts for the generation and stabilization of very small semiconductor QDs with sizes smaller than 1.5 nm,[24−35] we recently demonstrated that PbS QDs incorporated into zeolite Y films show high levels of resonant 3NLO activity.[36] Thus, their γ and β values are ~20 to 330 times higher than the highest values obtained from other QD−dielectric matrix systems[17−21] at 532 and 1064 nm, respectively. This achievement was made possible by a simultaneous finding that zeolite Y films can be grown on indium tin oxide (ITO)-coated glass plates (but not bare glass plates)[36,37] and the previous finding that surface coating of zeolite Y films with octadecylsilyl (ODC) groups effectively prevents the QD-incorporating zeolite Y films from imbibing moisture upon exposure to the atmosphere.[38] Otherwise, the zeolite framework immediately decomposes and the incorporated small active QDs aggregate into larger inactive QDs as a result of moisture adsorption.

After the above achievement, the next step would be to conduct research aimed at further improvements in the 3NLO activity of the incorporated PbS QDs by systematically varying the environments surrounding the QD guests. The outcomes of this research would then provide insights into the directions that future research should take.

In zeolites, the best method for systematically changing the environment surrounding the guests is to change the countercations systematically. In this way, the electric field

strength, pore volume, framework donor strength, cation acceptor strength, and so on can be sensitively and systematically changed. This is in fact one of the important advantages of using zeolites as the hosts for QDs, as no other dielectric matrices allow such parameters to be easily and systematically changed. Unfortunately, however, we have not been able to replace H$^+$ ions, the pristine cations produced during the formation of PbS QDs inside zeolite Y films (see below), with other cations.

PbS QDs are formed inside zeolite Y by treating dried, fully Pb^{2+}-exchanged zeolite Y with dry H$_2$S gas according to eq 2,

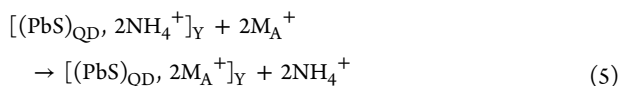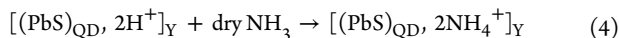$$[Pb^{2+}]_Y + dry\ H_2S \rightarrow [(PbS)_{QD}, 2H^+]_Y \quad (2)$$

where $[\ ]_Y$ represents zeolite Y, $(PbS)_{QD}$ represents PbS QDs, and 2H$^+$ represents the two H$^+$ ions charge-balancing the two negative (Al) centers in the zeolite Y framework instead of a Pb^{2+} ion. Accordingly, the newly prepared pristine PbS QD-incorporating zeolite Y films automatically contain H$^+$ ions in an amount twice that of Pb^{2+} ion. Under this circumstance, the environment of the zeolite pores is very acidic, with the pH often less than zero (section SI2).[29,30] This is why the pristine PbS QD-incorporating zeolite Y instantaneously undergoes framework decomposition upon exposure to the atmosphere, giving rise to aggregation of the incorporated PbS QDs as mentioned above. This is also the reason why replacement of the H$^+$ ions with other cations has not been possible, as the pristine PbS QD-incorporating zeolite Y cannot be exposed to the atmosphere before immersion into an aqueous solution for ion exchange. Surface coating with ODC groups also does not help ion exchange, as the highly hydrophobic ODC layer does not allow the entrance of aqueous solutions inside the zeolite interior.

In fact, H$^+$ ions in zeolites have been neutralized by passing dry NH$_3$ into H$^+$-containing zeolites.[39] Using this methodology with CdS QD-incorporating zeolite Y, we recently produced $[(CdS)_{QD}, 2NH_4^+]_Y$ by neutralizing the H$^+$ ions in $[(CdS)_{QD}, 2H^+]_Y$ with dry NH$_3$ (eq 3). Remarkably, studies of the atmospheric stability of $[(CdS)_{QD}, 2NH_4^+]_Y$ showed that the framework of this material did not undergo decomposition, and the small active CdS QDs did not aggregate into large inactive QDs, even when exposed to the moist atmosphere.[40]

$$[(CdS)_{QD}, 2H^+]_Y + dry\ NH_3 \rightarrow [(CdS)_{QD}, 2NH_4^+]_Y \quad (3)$$
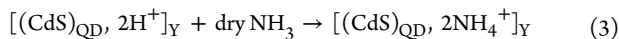
Stimulated by this finding, we similarly prepared $[(PbS)_{QD}, 2NH_4^+]_Y$ (eq 4) and subsequently investigated the possibility of ion exchanges of NH$_4^+$ with various alkali-metal ions (M$_A^+$ = Li$^+$, Na$^+$, K$^+$, Rb$^+$) in aqueous solution (eq 5).

$$[(PbS)_{QD}, 2H^+]_Y + dry\ NH_3 \rightarrow [(PbS)_{QD}, 2NH_4^+]_Y \quad (4)$$

$$[(PbS)_{QD}, 2NH_4^+]_Y + 2M_A^+$$
$$\rightarrow [(PbS)_{QD}, 2M_A^+]_Y + 2NH_4^+ \quad (5)$$

We now report that the ion exchange occurs very efficiently in aqueous solutions while the zeolite framework and the initially prepared PbS QDs remain intact and that the subsequently measured γ and β coefficients of $[(PbS)_{QD}, 2C^+]_Y$, where C$^+$ is the charge-balancing counterion, systematically increase by up to ~2.5 times at 532 and 1064 nm as C$^+$ is changed from H$^+$ to Li$^+$, Na$^+$, K$^+$, and Rb$^+$.

The preparation of $[(PbS)_{QD}, 2C^+]_Y$ is described in section SI3. The number of PbS units in zeolite Y was 32 per unit cell (the maximum amount for this zeolite is 33) regardless of C$^+$,

as shown by the compositions of $[(PbS)_{QD}, 2C^+]_Y$ in Table 1. Accordingly, each supercage contains four PbS units (i.e., a

Table 1. Compositions of $[(PbS)_{QD}, 2C^+]_Y$ Films Used in This Study

C$^+$	composition
H$^+$	Pb$_{32.1}$S$_{30.8}$(H)$_{67}$Al$_{67}$Si$_{125}$O$_{384}$
Li$^+$	Pb$_{32.0}$S$_{31.2}$(Li)$_{54.5}$(Na)$_{12.5}$Al$_{67}$Si$_{125}$O$_{384}$
Na$^+$	Pb$_{32.2}$S$_{30.9}$(Na)$_{67}$Al$_{67}$Si$_{125}$O$_{384}$
K$^+$	Pb$_{32.1}$S$_{31.1}$(Na)$_{8.2}$(K)$_{58.8}$Al$_{67}$Si$_{125}$O$_{384}$
Rb$^+$	Pb$_{32.0}$S$_{31.0}$(Na)$_{12.8}$(Rb)$_{54.2}$Al$_{67}$Si$_{125}$O$_{384}$
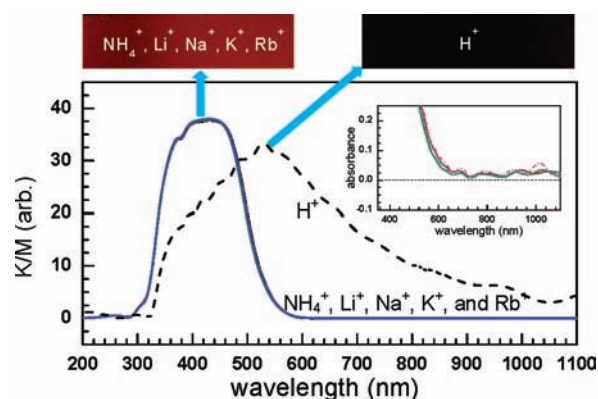
Figure 1. Diffuse reflectance spectra of $[(PbS)_{QD}, 2C^+]_Y$ for C$^+$ = NH$_4^+$, Li$^+$, Na$^+$, K$^+$, Rb$^+$, and H$^+$ (as indicated) after exposure to moisture and the corresponding colors (maroon and black for C$^+$ as indicated).

Pb$_4$S$_4$ unit). Their diffuse reflectance spectra (Figure 1) were identical regardless of C$^+$ (Figure 1), indicating that the sizes of QDs did not change during ion exchange. The colors of the films were also same (maroon; see Figure 1). This is a remarkable fact that provides zeolite scientists a variety of opportunities to explore diverse applications of zeolite-encapsulated QDs with different cation environments.

Furthermore, the fact that the absorption tail does not extend beyond 600 nm indicates that all of the PbS QDs exist in the isolated state.[41] This is indeed a very important phenomenon that allows us to compare the true effect of the cation type on the 3NLO activity of the intrazeolite PbS QDs, which would be impossible if the size and size distribution of the QDs changed simultaneously with changes in the cation type. In contrast, the dry pristine PbS QD-containing zeolite Y film $[(PbS)_{QD}, 2H^+]_Y$ immediately turned black upon exposure to the atmosphere (Figure 1) as a result of immediate decomposition of the framework and subsequent aggregation of the PbS QDs.

The non-Gaussian spectral shapes of $[(PbS)_{QD}, 2C^+]_Y$ for C$^+$ = NH$_4^+$, Li$^+$, Na$^+$, K$^+$, and Rb$^+$ indicate that the sizes of the PbS QDs are not uniform. Nevertheless, the measured lowest band-gap energy of PbS QDs was 2.3 eV. In view of the size−band gap energy relationship[42] and the size of a supercage, the size of the largest QD was estimated to be ~1.3 nm, which requires ~22 PbS units (section SI4); the size of the PbS QDs ranges from ~0.7 (four PbS units) (section SI4) to 1.3 nm (22 PbS units). This also indicates that not all of the supercages are occupied with PbS QDs.

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The γ and β values of $[(PbS)_{QD}, 2C^+]_Y$ measured at 532 and 1064 nm using mode-locked picosecond laser pulses with a pulse width of 50 ps (see section SI5 for experimental details) are listed in Table 2. The Z-scan data obtained from two

Table 2. 3NLO Activities of $[(PbS)_{QD}, 2C^+]_Y$ Films

	532 nm		1064 nm	
C^+	γ^a	β^b	γ^a	β^b
H^+	−284	5680	−121	−1256
Li^+	−352	6812	−174	−1945
Na^+	−481	9223	−217	−2244
K^+	−577	12031	−265	−2741
Rb^+	−704	15310	−319	−3242

^{a} In units of 10^{-12} cm^2/W. ^{b}In units of cm/GW.

different laser pulse powers at each wavelength are shown in sections SI6 and SI7. As noted, the magnitudes of γ and β progressively increase with increasing cation size while the signs remain unchanged. The negative γ values indicate that $[(PbS)_{QD}, 2C^+]_Y$ self-defocuses regardless of the type of cation at both wavelengths, and the degree of self-defocusing increases with increasing cation size. The positive and negative β values at 532 and 1064 nm, respectively, indicate that the PbS QDs behave as strong excited-state absorbers at 532 nm and optical bleachers at 1064 nm, and the sensitivity increases with increasing size of C^+. This is the first example demonstrating a systematic change in the 3NLO sensitivity of QDs by systematically changing the properties of a dielectric matrix.

Because the type of countercation sensitively affects the donor strength of the framework oxygen or the partial negative charge of the framework oxygen $(\delta_O)^{43}$(section SI8), we plotted the magnitudes of γ and β versus δ_O (Figure 2). The
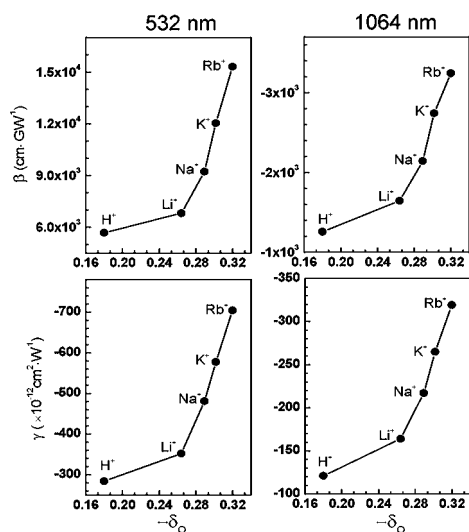

Figure 2. Plots of (top) β and (bottom) γ measured at (left) 532 and (right) 1064 nm vs Sanderson's partial negative charge of oxygen (δ_O).

results show that the magnitudes of the NLO coefficients increase exponentially with increasing δ_O despite the fact that their absorption spectra are the same.

In the semiconductor QD-based resonant 3NLO process, the NLO activity increases with a decrease in the absorption cross section for the transition from the ground state (S_0) to the first excited state (S_1) during the period of a laser pulse as a result of

an increase in the lifetime of a surface-trapped exciton (electron−hole pair) in each QD.[9] In this respect, we attribute the increase in 3NLO activity of $[(PbS)_{QD}, 2C^+]_Y$ with increasing size of C^+ to the increase in the lifetime of the surface-bound exciton due to the simultaneous increase in the electron donor strength of the framework oxygen and the electron acceptor strength of C^+, which intimately contact the PbS QDs (Figure 3).
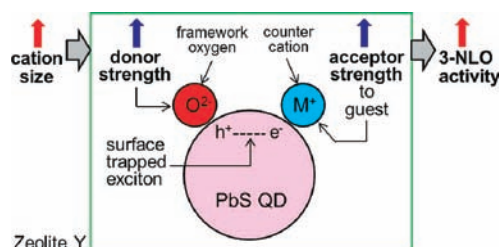
Figure 3. Schematic illustration of the increase in the 3NLO activity of a PbS QD in zeolite Y with increasing cation size.

Thus, when an exciton is bound to the surface of a QD, the hole (h^+) is likely to be positioned at the site that is in intimate contact with the framework oxygen, while the electron (e^-) is likely to be positioned at the site that is in intimate contact with a charge-balancing cation. Under this circumstance, the exciton lifetime would be expected to increase when the electron donor strength of the framework oxygen and the electron acceptor strength of the cation increase simultaneously. In zeolite, the simultaneous increase in framework oxygen donor strength and cation acceptor strength toward the guest occurs when the size of the cation increases. Although the former can be easily conceived, the latter is not so intuitive. However, this phenomenon indeed takes place in zeolite Y, as unambiguously demonstrated by the iodide-to-cation charge-transfer band, which is red-shifted with increasing size of C^+ because of the increase in acceptor strength of the cation as the size of C^+ increases.[44] This phenomenon occurs because the degree of protrusion of the countercation toward the supercage increases with increasing cation size (Figure 4), giving rise to a more intimate donor−acceptor interaction between the guest (iodide or PbS QD) and the cation.
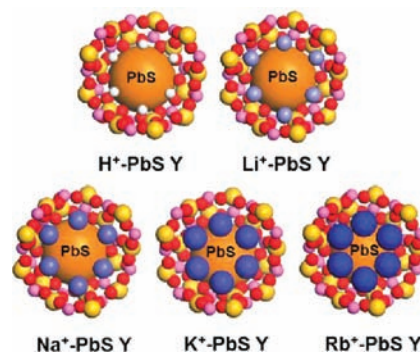
Figure 4. Schematic illustration of PbS QD-containing zeolite Y supercages with different countercations: H^+, Li^+, Na^+, K^+, and Rb^+ (see section SI9).

The fact that the 3NLO activity occurs by a resonant process at 532 nm is quite obvious. At 1064 nm, however, the absorbance is very small (Figure 1 inset), so it is not clear

whether the process is really resonant because the 3NLO sensitivity is much higher than its absorbance. Nevertheless, the open-aperture Z-scan method clearly showed that β is large and that its magnitude increases with increasing cation size, indicating that this is indeed a resonant process. The fact that the intrazeolite PbS QDs are very small also indicates that the process is resonant, as the probability of the nonresonant process increases with increasing QD size.[9] This is also a very interesting phenomenon because the related Cu, Ag, and Au nanoparticles dispersed in dielectric materials give no or very small β values at 1064 nm, although they give very high values (10^4–10^5 cm/GW) at their surface plasmon absorption wavelengths. This unique resonant 3NLO process of PbS QDs in zeolite Y at 1064 nm is due to their very high $S_0 \rightarrow S_1$ absorption cross section arising from their small size (<1.5 nm; the absorption cross section of a QD increases as its size decreases) and to the unique environment surrounding the PbS QDs with electron-rich oxide atoms and electron-poor cations.

We have thus found that H^+ ions in PbS QD-incorporating zeolite Y films can be readily exchanged with other cations without damage to the zeolite framework (and subsequent aggregation of the QDs) and that the 3NLO activity of the PbS QDs systematically increases with increasing countercation size. These results will promote applications of QD-incorporating zeolites in various fields and provide direction in the search for 3NLO materials with exceptional NLO properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures, compositions of zeolites, and Z-scan data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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