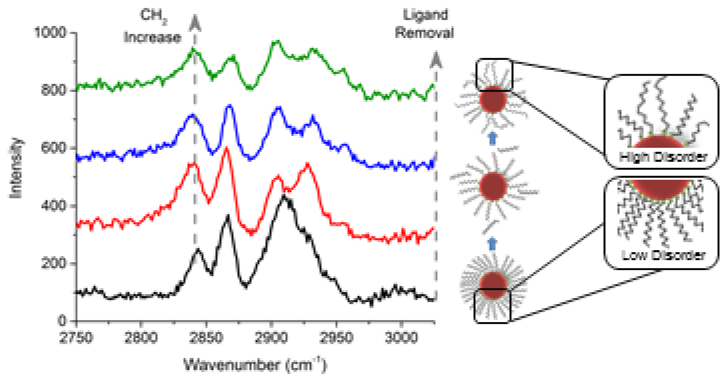
Graphical Abstract



Probing Ligand Removal and Ordering at Quantum Dot Surfaces Using Vibrational Sum Frequency Generation Spectroscopy

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Abstract

Hypothesis

Controlling nanomaterial interfaces for emerging technologies has driven the need to understand the molecular species located there; however, challenges arise using traditional analytical techniques to directly characterize the molecular structure and local environments of these interfacial species due to their low relative populations. We hypothesized that vibrational sum frequency generation (vSFG) spectroscopy will be uniquely sensitive to the chemical modification of nanoparticle surfaces that is obscured using traditional bulk sensitive methods.

Experiments

Octadecylamine ligands were removed from model CdSe quantum dots surface using a common precipitation-resuspension process using polar protic and aprotic nonsolvents. Vibrational spectra of the ligands at the surface were collected with vSFG to directly probe the ligand ordering and coverage. Photoluminescence (PL), optical absorption, NMR, and mass spectrometry measurements were conducted for comparison.

Findings

vSFG was found to be sensitive to subtle changes in ligand disorder over multiple precipitation-resuspension washes, and a limit to the number of ligand molecules removed from the surface and subsequent amount of disorder introduced to their packing was clearly observed. We also find that nonsolvents do not remain associated with the surface after washing.

Keywords:

Nonlinear spectroscopy, molecular ordering, vibrational spectroscopy, surface analysis

Introduction

The improvement of nano-synthetic methods has advanced the size consistency, shape, and optical performance of nanoparticle materials.[1] A large portion of the literature concerning the optimization of quantum dots (QDs) is dedicated to tailoring the interfacial layer on their exterior surfaces.[2] The choice of surface modification is integral to their performance because it dictates the solubility, electronic properties, and even the crystal structure of nanomaterials.[3-5] As such, surface modification impacts a wide range of areas including: compatibility and toxicity in biological imaging and biosensing, improved quantum efficiency for fluorescent probes, whitelight emission, and light harvesting applications.[6-10]

Synthetic routes for the chemical modification of CdSe quantum dot surfaces are well documented and typically consist of either coating the core semiconducting material with a shell of a different semiconductor material or introducing ligands that bind to the atoms on the exterior surface.[1, 2] The ligands can be characterized according to their interactions with the atoms at the surface of the nanoparticle and are described as L-type, X-type, or Z-type.[3, 11, 12] The presence and type of ligands on the surface can be varied either during or after synthesis via ligand exchange methods.[13-16] In recent years, there has been increased attention into how processing methods, including washing by precipitation and resuspension, can alter QD surface characteristics.[17-19] Specifically, this wash process is often a primary step in selecting a specific size QD and separating the quantum dots from the starting materials. Precipitation and resuspension typically involves the addition of a polar "nonsolvent", such as methanol or acetone, to generate a nanoparticle precipitate from solution which can then be transferred to a different solvent.[20, 21] Despite this commonly used approach, the number of times the process is repeated is often varied without a complete understanding of the effect on the remaining ligand structure on the nanoparticle surface. As L-, X-, and Z-type ligands exhibit different binding strengths to the nanoparticles, it is important to understand how standard synthetic steps affects the ligand coverage and molecular structure/ordering at the surface, as these species play a prominent role in applications.

Information about the effects of ligand modification on the particle is typically extracted from changes in photoluminescence (PL).[22-24] While PL is often used as a metric of surface quality, it only reports on the surface indirectly as the signal originates from the QD as a whole. The removal of ligands is expected to increase the number of dangling bonds as well as introduce gauche defects on the ligands themselves as they experience greater rotational freedom due to the reduced ligand packing. Substantially more information regarding disorder and heterogeneity in speciation could therefore be obtained by probing the surface species themselves.[25] As such, there has been efforts to directly probe surface moieties at nanoparticle surfaces using methods such as: scintillation counting,[26] NMR,[18] FT-IR,[27] Raman,[28] electronic absorption spectroscopy,[29] X-ray spectroscopies,[25] and thermogravimetric analysis.[30] While aspects of interfacial chemistry can be studied using these techniques, often times the intrinsic molecular information is still obscured or requires specific chemical labels (isotopes, etc.) to provide contrast between the surface and surrounding bulk species. Here, we apply vibrational sum frequency generation (vSFG) spectroscopy to probe the nascent vibrational transitions of the ligands themselves without the need for a complex sample preparation. The sensitivity of vSFG to interfacial ordering chemical composition allows for new insight into how surface ligand populations, and accompanying changes in ligand ordering, vary with systematic chemical modification of the QDs using standard precipitation-resuspension methods.

Materials and Methods

Sample Preparation

CdSe QDs of three different diameter sizes (4.6, 5.6, and 6.9 nm) suspended in hexanes were purchased from NN-labs (Fayetteville, Arkansas). These nanoparticles have an octadecylamine ligand coverage of approximately 20%, a Cd:Se ratio of 1:1, and a size distribution within 10% of the quoted size based on the expected absorption ranges 600 ± 10, 620 ± 10, and 640 ± 10 nm, respectively.[31] Ligands were removed from the quantum dots through a common precipitation and resuspension process,[32-35] by adding a 1:1 ratio of a polar nonsolvent to a 500 µL aliquot of the commercial quantum dots solution. Acetone (Sigma-Aldrich, ≥99%, USA) and methanol (Sigma-Aldrich, ≥99%, USA), which are common nonsolvents, were used as aprotic and protic solvents, respectively. The addition of the nonsolvent caused a precipitation of the QDs and the solutions were centrifuged at 6000 rpm for 10 min to facilitate complete separation. The supernatant was removed and the QDs were resuspended in fresh hexane to return the QDs to the original volume. A single iteration of this process was considered one wash and samples were washed one, two, three, or four times.

The resulting samples were diluted by a factor of nine in *n*-hexane (Honeywell, Chromasolv ≥97%, Germany) to a final volume of 4000 µL for characterization with vSFG, UV-Vis absorption, and photoluminescence. The final concentrations of these dilute solutions varied due to loss of QDs through the washing process but were in the range of 10^{13} – 10^{15} particles/mL as calculated from the UV-Vis spectra (see Figures 1a, S1, and Table S1) and are consistent with previous studies.[36, 37]

Sample Characterization

UV-Vis spectra were collected on a Cary 4E UV-Visible Spectrophotometer with a 1 cm path length and were used to measure QD concentration as well as monitor potential changes to the QDs core size. The first exciton peak amplitude was used to determine the concentration while the peak position was used to detect any changes to the core size.[17, 19, 31, 38, 39]

PL measurements were taken on the dilute samples to measure the effects of ligand removal on the QD PL intensity and were performed on a Fluorolog (Jobin Yvon). All samples were excited at 400 nm with a 2 nm excitation slit width. Emission spectra were corrected for the changes in solution concentration as determined from UV-Vis measurements. The resulting PL intensity at a given wavelength was then divided by the corresponding intensity of the unwashed sample to determine a concentration corrected change in PL (Tables S2, S3, S4).

Mass spectra on the supernatant solutions collected from the wash process were acquired using a SCIEX QTRAP® 5500 mass spectrometer. Proton NMR spectra of the QD solutions were acquired on a Varian VNMRS 500 MHz spectrometer. More detailed descriptions of these experiments and their results can be found in the SI.

Vibrational Sum Frequency Generation

vSFG is a nonlinear spectroscopy technique that makes use of two ultrafast pulses of light, one in the near infrared (NIR) and the other in the infrared (IR). The broadband IR pulse induces a polarization in the sample that is upconverted by a temporally overlapped narrowband NIR pulse to create a coherent second order polarization that oscillates and therefore radiates at the sum of the two incident laser frequencies. The measured intensity is proportional to the absolute square of the effective second order susceptibility, $\chi^{(2)}_{eff}$, and the driving light fields according to

$$I_{\mathrm{SFG}} \propto \left|\chi^{(2)}_{\mathrm{eff}} E_{\omega_{IR}} E_{\omega_{NIR}}\right|^2 \qquad (1)$$

where ω_{IR} and ω_{NIR} are the frequencies of the incident IR and NIR laser fields, respectively. For the case of vSFG, the effective second order susceptibility is the sum of resonant, $\chi^{(2)}_{res}$, and nonresonant, $\chi^{(2)}_{\mathrm{NR}}$, contributions:

$$\chi^{(2)}_{\mathrm{eff}} = \chi^{(2)}_{NR} + \chi^{(2)}_{res} = \chi^{(2)}_{NR} + \sum_k \frac{A_k}{\omega_{\mathrm{IR}} - \omega_k + i\Gamma_k} \qquad (2)$$

where ω_k, Γ_k, and A_k are the resonant frequency, linewidth, and amplitude of the k^{th}-mode. When the incident IR light is resonant with a molecular vibration, there is an enhancement of the radiated SFG, thereby mapping the vibrational spectrum. On account of the even-order field interaction, SFG from centrosymmetric and isotropic bulk media on average destructively interferes. In contrast, at an interface, where the symmetry is broken, appreciable signals can be observed. This means that SFG selectively probes the interfacial molecular species. The band positions, amplitudes, and peak ratios provide insight into the local organization, chemistry, and orientation of the interfacial molecules that is otherwise obscured by signal from the bulk in conventional linear spectroscopies.

The details of the optical setup and signal processing have been explained previously elsewhere.[40-43] Briefly, the output from a 1 kHz femtosecond regenerative amplifier (Spectra Physics Spitfire Pro) centered at 800 nm was split into two paths. A portion of this light was sent to a 4*f*-pulse shaper to produce ~1 ps pulses for use as the NIR up-conversion light. A majority of the amplifier output was routed to an optical parametric amplifier and difference frequency mixer (TOPAS-Prime) to produce the broadband IR pulses. The IR pulses were centered around 3450 nm (~2900 cm^{-1}) with a spectral bandwidth of about 300 cm^{-1} to probe the CH stretching region. The NIR and IR beams were brought together in typical reflection geometry with the beams focused on the sample at a 48° and 66° angle relative to the surface normal, respectively. The radiated vSFG was collimated, polarization resolved, and directed into a spectrograph (Acton SP2300*i*) equipped with a Pixis 256E (Princeton Instruments) CCD camera for detection. All QD vSFG spectra were taken with the SSP polarization combination, where the vSFG radiation was measured at S-polarized, the input NIR was S-polarized, and the input IR was P-polarized, in accordance with previous studies.[37, 44-46] vSFG spectra were collected by co-defining signal and background regions of interest (ROI) on the CCD camera. The signal ROI consisted of 10 vertical pixels, which were hardware binned to reduce readout noise, and 1024 horizontal pixels, that were hardware binned by a factor of 2 (to 512 pixels) that correspond to the wavelength of radiated light. The background ROI was subtracted from the signal ROI to remove stray light and the CCD camera intensity offset. This background subtracted spectrum was then scaled by a background subtracted reference spectrum obtained from an Au film using the PPP polarization combination to correct for the wavelength dependence of the mid-IR pulse.[40-43] NIR and IR powers incident on the sample were on the order of ~15 and ~4 mW, respectively. The dilute samples of CdSe QDs were drop cast onto quartz substrates for the vSFG measurements. The quartz substrates were cleaned before each trial with solutions of nanopure water (ThermoFischer Barnstead Nanopure. 18.2 MΩ-cm) and sodium hydroxide (Fischer Scientific, USA) followed by a rinsing with nanopure water and hexane. As expected, the cleaned substrates showed no vSFG response in agreement with previous work.[47] A single spectrum had an exposure of 5 minutes and was taken three times per trial. Multiple trials were collected at three to four spatial positions on the QD-quartz sample and averaged to ensure measurements are a representation of the whole sample and that potential spatial heterogeneities (*e.g.* coffee rings) do not impact the results. No photodegration was observed over any of the trials or any of the different spatial positions.

Data Analysis

Analysis of the vSFG spectra was performed using custom LabVIEW and Python scripts. The analysis consists of fitting each of the vSFG spectra to Equations 1 and 2 using four Lorentzians and a nonresonant contribution; [37, 44, 47] additional details are included in the SI along with a comprehensive summary of the fitting parameters. An average of at least three trials were used to tabulate all values.

Results and Discussion

Initial optical absorption measurements were taken to ensure that the only modification to the quantum dots were due to the surface ligand removal and not from etching the metal chalcogenide surface. Figure 1a shows the UV-Vis spectra for the 4.6 nm QDs after different numbers of washes (UV-Vis spectra for the other size samples can be found in Figure S1). The peak position of the first exciton band around 600 nm does not change substantially between washes. This matches the expectation that removal of the octadecylamine which are L-type ligands does not induce surface etching.[18] It should be noted, however, that changes in the amplitude of the peaks indicates a decrease in quantum dot concentration due simply to loss during the washing steps. Furthermore, changes in the baseline are indicative of aggregation after washing (*i.e.* more scattering from larger particles) and is consistent with the loss of ligands that stabilize the particles in solution.

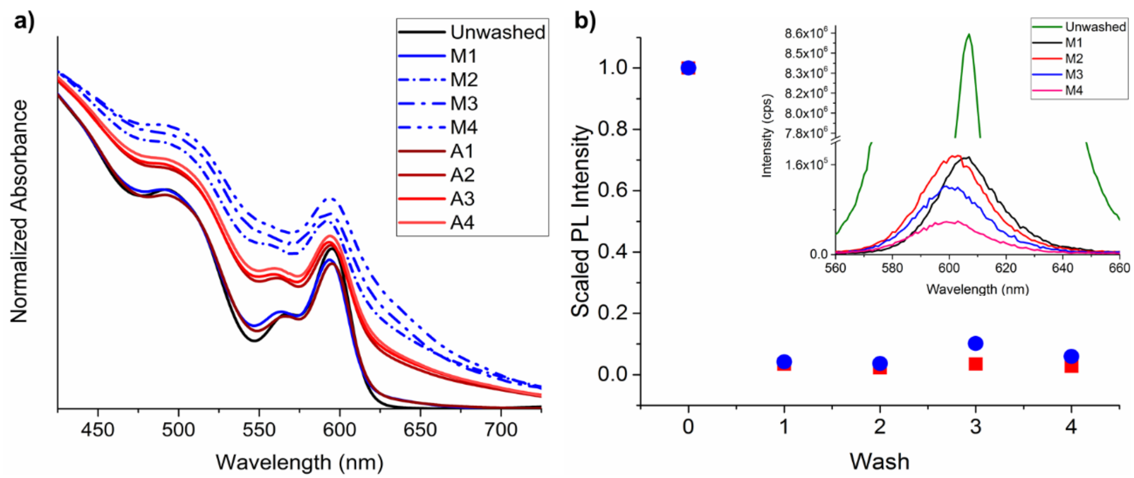

Figure 1. a) UV-Vis spectra for 4.6 nm CdSe series. Spectra are labeled by the nonsolvent ("A" for acetone and "M" for methanol) and the number of washes performed on the sample. UV-Vis spectra have been normalized at 400 nm for comparison. b) Concentration corrected PL intensities are plotted as a function of wash step; red squares represent a nonsolvent of acetone while the blue circles are for methanol. Inset shows raw PL data for the methanol washes.

Ligands, as stated previously, are important regulators of QD optical properties by coordinating with atomic species at the surface to prevent the formation of surface trap states. The removal of ligands opens up nonradiative pathways that result in a decrease in PL. This phenomenon has been described extensively in literature.[4, 13, 22, 23, 48-53] In order to assess these changes over our washing cycles, PL measurements were made using the same samples employed in the linear absorption and the vSFG measurements described below. Emission peaks were centered at 610, 630, or 650 nm depending on the size of the particle. For all the samples studied, a sharp drop in PL after the first washing was observed, as shown in Figure 1b for 4.6 nm QDs, where the PL intensity for each sample was corrected for the decreasing concentration then divided by the PL intensity of the unwashed sample (as shown in Tables S2-4). The complete set of acquired PL data can be found in the SI (Figures S2-6). Even though PL is the most common spectroscopic method to assess the effects of ligand modification, the link between the PL quantum yield of the bulk and the surface ligation is not well understood. Specifically, we can consider three possible mechanisms as sources of the decreased PL intensity: (1) an increased number of surface trap states due to dangling bonds at the sites of ligand loss, (2) aggregation and (3) the adsorption of nonsolvent molecules to the surface.[4, 17] Some support for the first mechanism can be seen in a few of the PL spectra (Fig. S5) as the rise in signal on the red edge is likely due to emission from trap states which has been well documented by others. This also matches recent theoretical work which implicates reduced coordination of surface atoms as the primary source of trap states on CdSe quantum dots. Turning then to the contribution of the other two mechanisms, UV-Vis can provide some information on the extent of aggregation in our samples. Specifically, as aggregation in the sample increases, the resulting larger particles will scatter more light resulting in an increased baseline signal as is apparent in Fig. 1a. This is not unexpected as one of the primary roles of the ligands is to facilitate solvation of the particles in solution, however, it is only significant for the second through fourth washes for both nonsolvents. Further, while the UV-Vis baselines for the two nonsolvents are different, with methanol appearing to result in more aggregation, there is no significant different in the PL for two washing conditions. Despite these observations, however, we cannot rule out aggregation as a significant source of decreased PL intensity as the UV-Vis does indicate the presence of aggregates after washing. In order to investigate the role of the third mechanism, however, requires the use of a technique that can provide chemically specific information for only those species at the surface, namely vSFG as discussed below. Overall, the need for additional techniques demonstrates that while PL is a facile method for quantifying optical properties of these materials, it does not have enough chemical fidelity to provide a comprehensive picture of the surface interactions and alterations.

In an attempt to quantify the change in ligand coverage on the surface of the QDs, ^{1}H NMR experiments were conducted as has been done previously.[50, 54-56] NMR spectra were collected for QD samples at each washing step, but no obvious features were observed that could be conclusively attributed to the ligands (See SI). This was due to the large difference in concentration between the hexane solvent and the octadecylamine ligands and highlights the limitation of using NMR for our relatively simple, model system of a commercially-available hydrocarbon amine in a standard organic solvent. Because of the NMR experiments' inability to quantify the ligand surface coverage, mass spectrometry was performed on the supernatants that were removed during the washing steps to corroborate the removal of the octadecylamine ligand. As seen in Figure S14, this data confirms the presence of octadecylamine in these solutions confirming that these ligands are originally attached to the surface and washing does in fact remove them. This qualitative finding also agrees with the vSFG results discussed below.

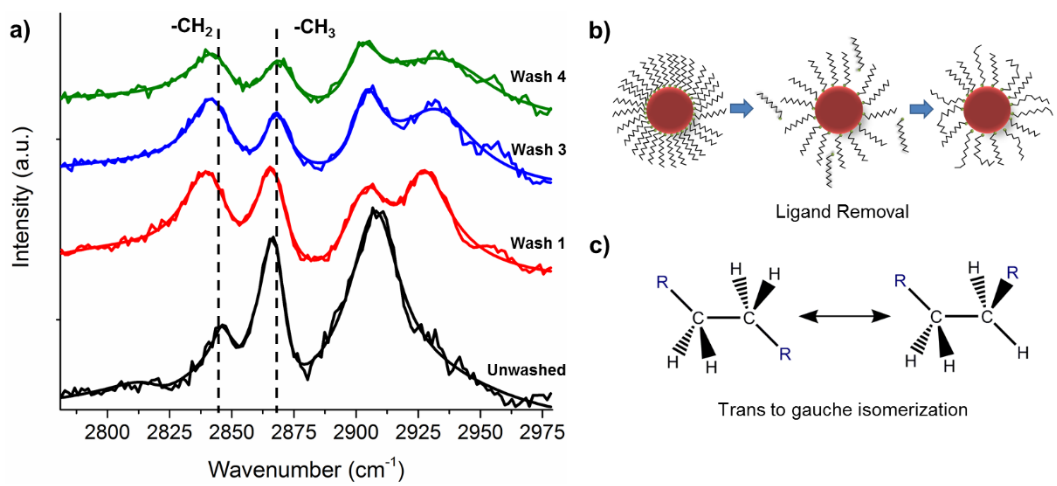

Figure 2. a) Representative vSFG spectra for 4.6 nm CdSe quantum dots washed with methanol. Spectra from bottom to top correspond to zero, one, three, and four washes, respectively. The fits for the spectra are shown on top of the spectra. Spectra are separated vertically for clarity. The symmetric stretches used for the analysis shown in Figure 3 are highlighted. b) Illustration of ligand removal effects on ligand configuration. Ligand removal allows for configuration changes from trans to gauche in the alkyl chain of the octadecylamine (as shown in c).

The vSFG spectra shown in Figure 2 have four distinct features near 2846, 2868, 2903, and 2929 cm^{-1}. The symmetric methylene stretch ($-CH_2$,*ss*) is identified around 2846 cm^{-1} and the symmetric methyl ($-CH_3$,*ss*) stretch is around 2868 cm^{-1}, while the asymmetric methylene and asymmetric methyl stretches ($-CH_2$,*as* and $–CH_3$,*as*) are tentatively identified at 2903 and 2929 cm^{-1}, respectively. The symmetric stretch values closely resemble those reported previously for alkyl chains of similar size.[37, 44, 46, 47, 57, 58] Due to ambiguities in a precise assignment of the asymmetric bands arising from Fermi resonances from the symmetric stretches, we choose not to use these bands in analysis of ligand ordering at the QD interfaces and thus they are not the focus of this work. It should be noted that broadening and shifting of peaks was observed in all sample sets between washes, quantum dot size, and nonsolvent (further information in the SI). This broadening is most likely due to changes in the surface chemical environment resulting from both the removal of ligands and drying on the surface of the quartz substrates. To the authors' knowledge there are studies which show blue shifting of the stretches[27, 30] but no studies which observe the red shifting that is also apparent in our data. It is possible that physical interaction between the solvation environment/substrate/particle is responsible, but we do not definitively assign the origin of the shift. As seen in Figure 2, the more washes the quantum dots undergo the smaller the difference in amplitude between the $-CH_2$,*ss* and the $-CH_3$,*ss* peaks. The same trend can be gleaned from the asymmetric region as well; however, this region is more complicated to analyze due to the number of peaks and complicated assignments in this region. There are no obvious signals in the vSFG spectra that can be attributed to methanol (symmetric methyl stretches around 2825 cm^{-1}), as seen in Figure 2, or acetone (symmetric methyl stretch between 2920 and 2925 cm^{-1}), as seen in Figure S19.[46, 59] This indicates weak adsorption or poor ordering of nonsolvents at the surface. For methanol specifically, this is in contrast to some previous studies which have invoked surface association. An explanation of this behavior arises from the fact that on resuspension of the precipitated nanocrystals the equilibrium of adsorbed nonsolvents at the particle surface shifts to displace these species into the bulk solution. Overall, this leads to new insight into the origin of the decrease in PL intensity (Figure 1b) as it removes the mechanism of quenching by nonsolvent adsorption from being considered as a significant contributor.

By analyzing the changes in the vSFG relative intensities for the methylene and methyl symmetric stretches in more detail (see Fig. 2a), we can examine the ligand ordering at the interface as a function of wash. This is because the ratio of these features describes the interfacial conformations of the remaining ligands bound to the surface. To elaborate, the packing of ligands on the surface of unwashed QDs will primarily be based on the ligand length, number density, and size of the QD such that each ligand tail will be confined to a limited spatial footprint in an all-trans conformation allowing for maximum ligand coverage at the particle surface (Fig. 2b), much like a self-assembled monolayer. The presence (and increase) of methylene vSFG spectral features, which should be weak for alkyl chains such as these, due to in plane symmetry, is indicative of gauche conformers at the interface as shown in Fig. 2c.[36, 37, 44, 47, 60, 61] In contrast, vSFG signal from the terminal methyl symmetric stretch is present despite configuration of the alkyl chain; thus, by comparing the ratio of methylene to methyl stretch the amount of disorder in the ligands can be evaluated while accounting for changes in overall coverage. A relationship between nanoparticle size and ligand disorder was previously demonstrated using gold nanoparticles that showed an increase in ligand ordering as the diameter increased.[36, 37] Smaller particles (those <4.4 nm, i.e., QDs) have less efficient packing due to the smaller facets and overall higher curvature of the surface. Above the 4.4 nm size the packing is determined by the chain length to radius ratio. In the case of CdSe QDs, it has also been shown that the surface Cd:Se ratio will affect ligand ordering with a higher ratio of Cd:Se having more disorder.[47] Our study shows for the first time that washing the QDs also impacts the ligand ordering at the surface.

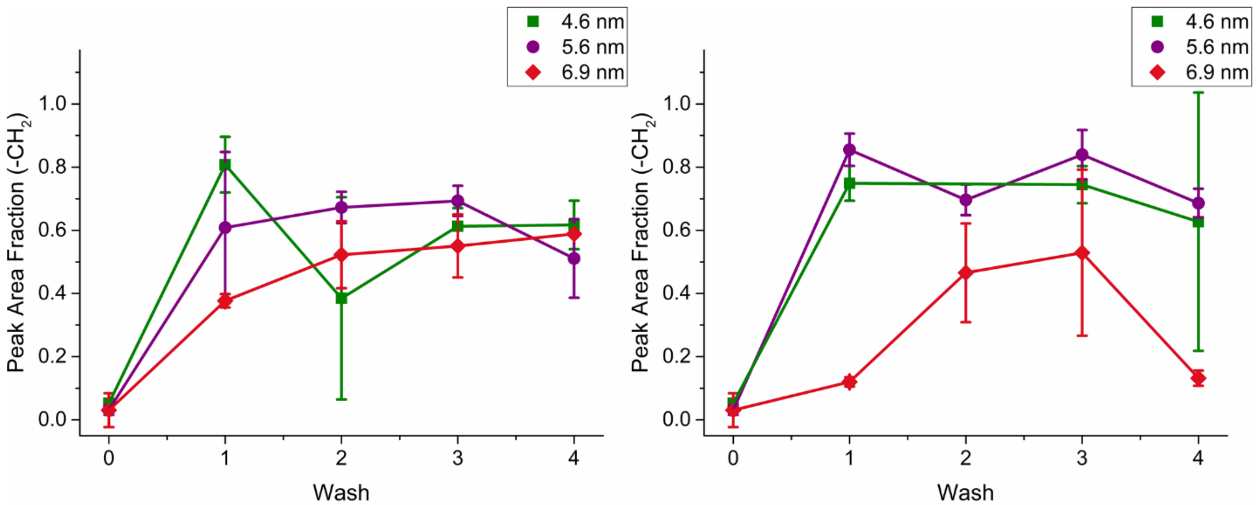

Figure 3. Peak area fraction of symmetric methylene stretches to both symmetric stretches determined using acetone (left) and methanol (right) as the nonsolvent, respectively. Error bars represent the standard deviation of the averaged ratio from different spatial positions.

Following the procedure of Barrett and Petersen, the peak ratio of the methylene to methyl ratio was calculated by using the peak area of the symmetric methylene ($-CH_2$,*ss*) stretch divided by the sum of both the symmetric peak areas ($-CH_2$,*ss* and $–CH_3$,*ss*).[44] The peak area was calculated by multiplying the amplitude of the fitted peak by its extracted width. Using the peak area instead of the amplitude alone allows for the determination of these ratios while explicitly accounting for peak broadening. These ratios are shown in Figure 3 as a function of number of washes. When comparing the peak fraction of $-CH_2$,*ss*, similar trends for both nonsolvents were observed. The change in peak fraction of $-CH_2$,*ss* from the zeroth to the first wash shows a clear increase in the occurrence of the methylene bands and therefore an increase in ligand disorder (Figures 2 and 3). This indicates that ligand removal is accompanied by an increase in the rotational volume allowed per ligand.[36] As the number of washes increases there are still subtle changes in the amount of disorder introduced to the ligands as the peak fraction area of $-CH_2$,*ss* levels off (for instance for th 6.9 nm QDs washed with acetone). These subtilties were not captured by PL measurements (Figure 1b) that only indirectly report on the surface chemistry or by NMR that was blind to the interfaces in the native solvent all together (SI). Since vSFG signal from the ligands is still present through the fourth wash, it is clear that some ligands are still present at the QD surface and that the largest change in the ordering occurs during the initial wash. This is both expected and surprising for different reasons: first, the weak coordination to the surface might indicate that the ligands would be quickly and completely displaced which is not observed in our vSFG measurements – while the largest change in ordering happens from unwashed particles to washed particles, signal from the native ligands persisted even after 4 washes. This means that one never really removes all the ligand. L-type ligands have a weaker dative bond; therefore the removal of these ligands is straightforward, which is supported by previous studies showing strong ligand removal during the precipitation-resuspension of nanocrystals and smaller subsequent removals beyond one wash.[17, 19] For these reasons, the peak fraction ratio is explained by a ligand removal process where the first wash has a significant impact and continued washing has subtle effects and with small changes to the confirmation of the chain of the ligands. Vibrational SFG measurements on mixed monolayers of octadecyltrichlorosilane (C18) and dodecyltrichlorosilane (C12) on silica substrate by Barrett and Petersen showed similar sensitivity to disorder.[44] Our results show that continued removal of these ligands does not result in increasing disorder- there is a limit to the overall disorder that can be introduced to the QD interface.

Conclusion

Here we demonstrated the use of vibrational sum frequency generation spectroscopy to characterize the removal of ligands from the surface of CdSe quantum dots. This is the first work to extend the application of this technique to study disorder as it relates to ligand removal and not only size.[36, 37, 47] Overall these experiments provide two novel findings: first that there is a limit to the number of ligands that can be removed and subsequent disorder that is introduced for multiple precipitation-resuspension washes, and second that there is no evidence of nonsolvent adsorption. Both of these findings are observed to be relatively impervious to the size of the QD and the choice of protic or aprotic nonsolvent. Our result that some octadecylamine ligands still remain on the CdSe QD after multiple washing steps matches previous work attempting to remove other ligands from CdSe surfaces and is also reminiscent of the ongoing debate in the literature regarding the removal of citrate from the surface of gold nanoparticles. By seeing similar behavior for octadecylamine ligands on CdSe here, we provide more evidence to the growing body of literature showing complete ligand removal is a significant widespread concern for nanoparticle systems. The work we present here highlights how vSFG can be a critical tool in the study of this problem with future work aimed studying X-type ligands that bond more strongly to the QD surfaces and alternative nonsolvents, such as ethanol or acetonitrile, which have less impact on PL.

Declaration of Interest: None

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