

Mercaptopyridine Surface-Functionalized CdTe Quantum Dots with Enhanced Raman Scattering Properties

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We report that 3 nm diameter CdTe quantum dots can generate enhanced Raman scattering. The Raman signal of 4-mercaptopyridine (4-Mpy) adsorbed on CdTe quantum dots shows a 10^4 enhancement compared with that of bulk 4-Mpy. The enhanced phenomenon based on CdTe quantum dots also provides new insight to help understand the enhancement mechanism. A charge-transfer mechanism is most likely responsible for the observed enhancement, since plasmon resonances are ruled out. This study points to the possibility of using quantum dots, with chemisorption in some important practical systems, such as the application of quantum dots as nanosized building blocks and markers in biological imaging.

Introduction

Considerable effort has been directed toward the investigation of low-dimensional semiconductor nanostructures due to the rich physical phenomena they exhibit that give rise to numerous potential applications.^{1,2} In particular, when the particle size is reduced below the Bohr radius of the lowest lying exciton state, dramatic changes to the material's optical properties are effected. The quantum confinement of conduction electrons impart many novel properties to these nanostructures such as single-electron-transistor properties, enhanced nonlinear optical activities, and increased band gap. However, there are few reports about semiconductor quantum dots with enhanced Raman scattering properties. The fact that the size of quantum dots may readily be controlled, resulting in variation of their optical and electrical properties, makes them suitable as a basis for novel nanoscale electronic and optoelectronic devices,^{3,4} especially the use of fluorescent markers in biological imaging.^{5,6} However, such dramatic fluorescence tends to obscure the Raman signal, thus limiting the possible applicability. Whenever the technique of Raman spectroscopy is applicable, an enhanced Raman signal combined with suppression of fluorescence makes it ideal for high-resolution, yet sensitive molecular detection.

Normally Raman scattering from molecules adsorbed on surfaces is too weak to be detectable. In order to overcome these problems, interest in enhanced Raman scattering is growing at present. The surface-enhance Raman scattering (SERS) effect is characterized by an increase in the Raman intensity by many orders of magnitude for species adsorbed on rough metal surfaces, even for the detection of a single molecule.^{7,8} As a result, SERS has become a powerful analytical tool for determining chemical information for molecules on metallic substrates.⁹ The most critical aspect of performing a SERS

experiment is the choice or fabrication of the ideal substrate.^{10,11} Only three noble metals, Au, Ag, and Cu, have been found to provide such large enhancements, although there are also reports concerning weaker enhancements from transitional metals.¹² Until recently it was felt that SERS could not be observed on semiconductor substrates. However, several reports have shown that a surface enhancement effect can in fact be observed in such systems, although with generally lower enhancements than in metals. The first reports involved systems such as InAs/GaAs quantum dots,¹³ GaP nanoparticles,¹⁴ and TiO₂.¹⁵ More recently, observations have been reported in ZnO,¹⁶ ZnS,¹⁷ CdS,¹⁸ and CuO¹⁹ colloidal nanoparticles. There is every reason to believe that still more systems will be investigated in the future.

In this paper, we obtain an enhanced Raman signal from 4-mercaptopyridine (4-Mpy) adsorbed on 3 nm diameter CdTe quantum dots. A 10^4 Raman enhancement is achieved. A charge-transfer mechanism is most likely responsible for the observed enhancement, since plasmon resonances are not excited at the wavelengths used.

Experiments

Sample Preparation. *Synthesis of 2-Dimethylaminoethanethiol Hydrochloride Capped CdTe Quantum Dots.* Synthesis of 2-dimethylaminoethanethiol (2-DMA) capped CdTe quantum dots follows a similar procedure for preparing CdTe quantum dots stabilized by 2-aminoethanethiol which is described in detail elsewhere.²⁰ In brief, freshly prepared oxygen-free NaHTe solution was added to N₂-saturated aqueous solution of 2-DMA and Cd(ClO₄)₂·6H₂O at pH 5.5. The molar ratio of Cd²⁺:Te²⁻:2-DMA was 1:0.5:2.4. The resulting mixture was then subjected to reflux for 2 h. In this way, 2-DMA capped CdTe quantum dots were obtained.

Synthesis of 4-Mpy Surface-Functionalized CdTe Quantum Dots. The synthesis of 4-Mpy surface-functionalized CdTe quantum dots follows a similar procedure for preparing 2-DMA

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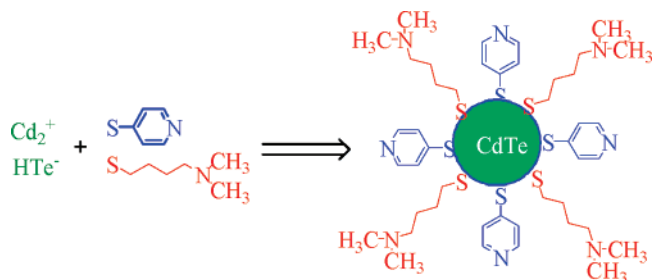


Figure 1. Model of 4-Mpy surface-functionalized CdTe quantum dots.

capped CdTe quantum dots. Only the stabilizing agent of 2-DMA was substituted by a mixture of 2-DMA and 4-Mpy. In a typical synthesis of 4-Mpy surface-functionalized CdTe quantum dots, 1.5 mL of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1 M) was added to 100 mL of water. Then freshly prepared oxygen-free NaHTe solutions was added to a slightly basic N_2 -saturated $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ solution (1.5×10^{-3} M) in the presence of DMA and 4-Mpy as stabilizing agents at pH 5.5. The molar ratio of Cd^{2+} : Te^{2-} :2-DMA:4-Mpy was fixed at 1:0.5:1.2:1.2. The resulting mixture was then subjected to reflux for 2 h to obtain CdTe quantum dots. If all 4-Mpy associates on the CdTe quantum dots, the maximal concentration of 4-Mpy will be 1.8×10^{-3} M. The crude solutions of the quantum dots were dialyzed against water to remove excess thiols and ions. Transmission electron microscopy (TEM) shows that the size of synthesized semiconductor quantum dots is about 3 nm. The model of 4-Mpy surface-functionalized CdTe quantum dots is shown in Figure 1.

Previous studies show that mercapto compounds may be used effectively as capping agents to prepare CdTe quantum dots. The mercapto compounds include 2-dimethylaminoethanethiol (2-DMA) and 2-aminoethanethiol. UV absorption and X-ray diffraction (XRD) confirm the formation of CdTe quantum dots.^{21,22} In addition, it has been well-established that mixed ligands may be used to prepare and stabilize nanoparticles.²³ We chose 4-Mpy as stabilizer because it along with thiophenol has been shown to be very effective in stabilizing nanoparticles.²³ UV absorption is used to confirm the formation of CdTe quantum dots.

Preparation of 4-Mpy Surface-Functionalized CdTe Powder. CdTe powder was prepared by a previously published method of size-selective precipitation. Briefly, a portion of as-prepared 4-Mpy surface-functionalized CdTe quantum dots (3 nm) is concentrated 5 times using a rotary evaporator. Then, 2-propanol is added dropwise under stirring until the solution becomes slightly turbid. The turbid dispersion is left stirring for a further 20 min, and the precipitate containing the fraction of 4-Mpy surface-functionalized CdTe is isolated from the supernatant by centrifugation. Thus 4-Mpy surface-functionalized CdTe powder was obtained.

Preparation of Samples for Raman Measurement. The 4-Mpy surface-functionalized CdTe quantum dot solution was incubated in a U-type glass capillary for Raman measurement. The U-type glass capillary device was devised by our laboratory.²⁴ For comparison, 0.2 M bulk 4-Mpy solution was examined using the same U-type glass capillary device.

The 4-Mpy surface-functionalized CdTe powder was measured on a Si wafer.

Instruments. Raman spectra were obtained with a Renishaw Raman system Model 1000 spectrometer. The 514.5 nm radiation from a 20 mW air-cooled argon ion laser was used as the exciting source. The laser power at the sample position was typically 2.0 mW for 4-Mpy surface-functionalized CdTe

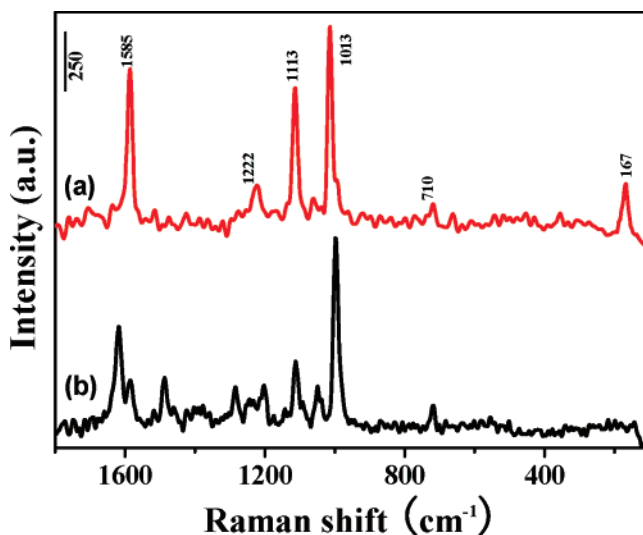


Figure 2. Raman spectra of (a) 4-Mpy surface-functionalized CdTe quantum dots and (b) 0.2 M bulk 4-Mpy solution.

quantum dots and powder. Data acquisition was the result of five 30-s accumulations for CdTe quantum dots and powder.

UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer, and the slit width was set at 2 nm.

Fluorescence experiments were performed using a Shimadzu RF-5301 PC spectrofluorimeter, and the slit width was set at 5 nm at room temperature under ambient conditions.

Transmission electron micrographs were recorded by a JEOL-2010 electron microscope operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) was investigated by using a VG ESCALAB MK II spectrometer with a Mg KR excitation (1253.6 eV). Binding energy calibration was based on C 1s at 284.6 eV.

Results and Discussion

Raman Spectra of 4-Mpy Surface-Functionalized CdTe Quantum Dots and Powder. The Raman spectrum of 4-Mpy surface-functionalized CdTe quantum dots in solution and that of 0.2 M bulk 4-Mpy solution are illustrated in Figure 2. As is shown in Figure 2a, this spectrum consists of several observable peaks located at 1585, 1222, 1113, 1013, 710, and 167 cm^{-1} , respectively. The corresponding lines located at 1585, 1222, 1113, 1013, and 710 cm^{-1} are intrinsic to 4-Mpy, while that at 167 cm^{-1} is a semiconductor mode. Since the spectrum from the quantum dots differs somewhat from the solution spectrum, it is likely that the signal comes almost completely from the 4-Mpy molecules adsorbed on the CdTe quantum dots rather than any free 4-Mpy molecules remaining in solution. Assuming all 4-Mpy associates on the CdTe quantum dots, the maximal concentration of 4-Mpy is 1.8×10^{-3} M, and at this concentration Raman signals of 4-Mpy are too weak to be observed. With the same experimental conditions, only when the concentration of 4-Mpy in aqueous solution is above 0.2 M can the equivalent intensity Raman signals be detected. This suggests that the Raman signals measured on the CdTe quantum dots originate from 4-Mpy molecules adsorbed, and that the intensity observed is greatly enhanced by attachment to the surface. The band at 167 cm^{-1} corresponds to the longitudinal optical (LO) phonon mode of CdTe. In the bulk the LO phonon mode of CdTe is 171 cm^{-1} . The shift in frequency of this band is consistent with that of a spherical microcavity with CdTe quantum dots.²⁵ We should note also that this mode is too weak to be seen in our samples without adsorption of 4-Mpy. This indicates that the

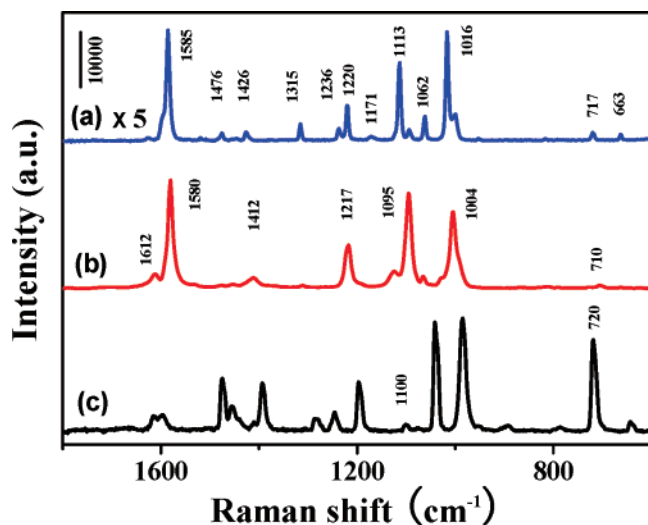


Figure 3. Raman spectra of 4-Mpy adsorbed on (a) CdTe powder and (b) silver colloid. (c) Normal Raman spectra of bulk 4-Mpy powder.

adsorption of the surface layer including 4-Mpy enhances the intensity of this mode as well.

For comparison, the Raman spectra of 4-Mpy adsorbed on CdTe powder, 4-Mpy adsorbed on silver colloids, and solid 4-Mpy powder are depicted in curves, a, b, and c, respectively, of Figure 3. The Raman spectrum of 4-Mpy adsorbed on CdTe powder, similar to that on silver colloid, is considerably different from that of bulk 4-Mpy. For example, in Figure 3a,b, there was exhibited a marked downshift of the $\nu(\text{C}-\text{S})$ mode at 717 cm^{-1} and a dramatic increase in intensity of the $\nu(\text{C}-\text{S})$ mode at 1113 cm^{-1} in comparison with the Raman spectrum of bulk 4-Mpy. A similar downward shift and enhancement have been observed for 4-Mpy adsorbed on other metal substrates such as Au,²⁶ Ag,^{27–29} and Pt³⁰ surfaces, which has been interpreted by coordination of 4-Mpy with the metal surface through the sulfur atom. This leads to the conclusion that 4-Mpy may be adsorbed on CdTe powder via the S atom.

In addition, the Raman spectrum of 4-Mpy adsorbed on CdTe powder is considerably different from that on silver colloids. First, a prominent characteristic is that the width of spectral lines is narrower in the Raman spectrum of 4-Mpy adsorbed on CdTe powder. Commonly, the bands of the SERS spectrum from metals are wider than those of bulk spectrum. However, the Raman spectrum of the molecule adsorbed on the semiconductor does not follow this rule. The reason can be tentatively ascribed to the narrower distribution of CdTe quantum dots compared with the silver nanoparticles or, alternatively, a preresonance effect.

Second, both the frequencies and relative intensities of Raman spectra of 4-Mpy adsorbed on CdTe powder vary considerably compared from those on silver colloids. Some lines of 4-Mpy are especially sensitive to the environment of the molecule. The Raman bands at 1426 , 1315 , 1113 , 1016 , and 663 cm^{-1} among others show a remarkable shift compared with those on metal substrate (Table S1). Most notably the ring-breathing C–S mode at 1113 cm^{-1} is observed at 1095 cm^{-1} on Ag. These frequency shifts are reasonably attributable to the difference between the S–Ag and S–Cd bonds. It is clear from the changes in the Raman peak that the vibrational frequency of the adsorbed molecule is dependent on the nature of the substrate.

Modified Optical Properties. Strong fluorescence from 2-DMA capped CdTe quantum dots hides any possible Raman vibrational spectrum. However, the presence of surface 4-Mpy ligand quenches the emission of 4-Mpy surface-functionalized

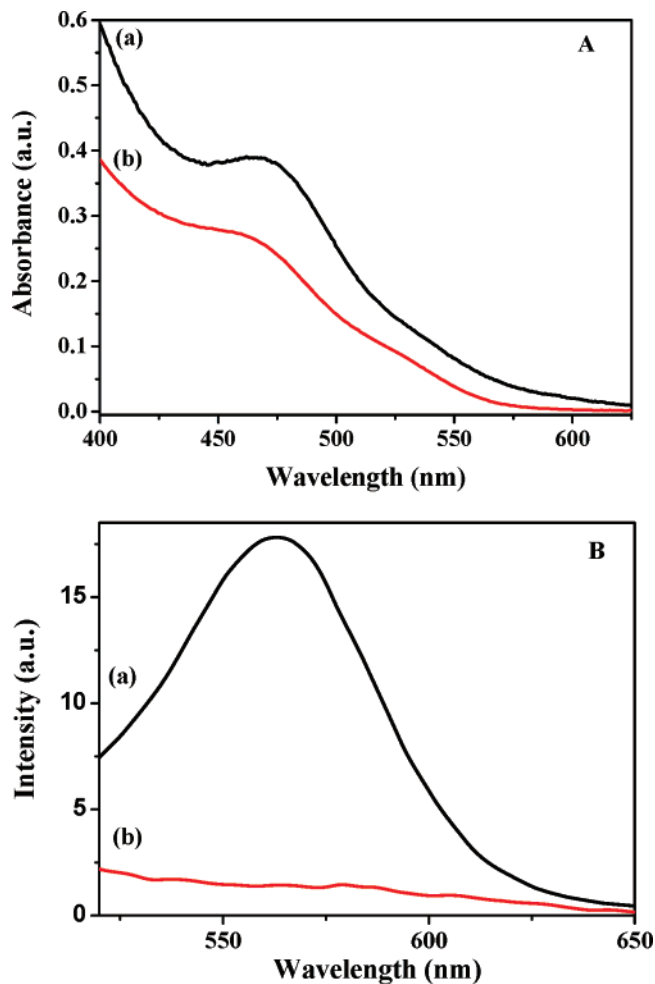


Figure 4. (A) Absorption spectra and (B) photoluminescence spectra of (a) 2-DMA capped CdTe quantum dots and (b) 4-Mpy surface-functionalized CdTe quantum dots (excitation at 470 nm).

CdTe quantum dots. Absorption and photoluminescence measurements were carried out to study the effect of addition of 4-Mpy ligand on the optical properties of CdTe quantum dots in aqueous solution (Figure 4). Curves a and b in Figure 4A show the absorption spectra of 2-DMA capped CdTe quantum dots and 4-Mpy surface-functionalized CdTe quantum dots, respectively. The absorption spectrum for 2-DMA capped CdTe quantum dots shows an absorption band at 470 nm . The absorptive peak of 4-Mpy surface-functionalized CdTe quantum dots exhibits a slight shift. The strong mixing of the CdTe quantum dots and 4-Mpy electronic states results in modified optical properties exhibiting broadened peaks and a slight shift.

The effect of 4-Mpy surface functionality on the luminescence of the CdTe quantum dots is of considerable interest. The changes observed in the absorption spectra, in the presence of 4-Mpy ligand, are accompanied by quenching of the luminescence of 4-Mpy surface-functionalized CdTe quantum dots (Figure 4B). Quenching of the emission by 4-Mpy molecules is expected via destruction of the surface-trapped state by electron capture. This behavior resembles the super quenching effect of thiol capping on the exciton luminescence of CdTe and CdSe quantum dots,³¹ CdS microclusters²³ by highly efficient charge transfer.³² Both absorption and emission spectra exemplify the large effect of 4-Mpy ligand on CdTe quantum dots in this new system, providing further evidence of the strong bonding of the 4-Mpy to the CdTe quantum dots.

Estimation of the Enhancement Factor. To evaluate the effect of CdTe quantum dots on the Raman spectra of an

adsorbate, it is useful to estimate the enhancement factor. The enhancement factor (EF) for 4-Mpy surface-functionalized CdTe quantum dots was calculated according to the following expression:³³

$$\text{EF} = \frac{I_{\text{ERS}}}{I_{\text{Raman}}} \frac{[M_{\text{b}}]}{[M_{\text{ads}}]}$$

where $[M_{\text{b}}]$ is the concentration of molecules in the bulk sample and $[M_{\text{ads}}]$ is the concentration of adsorbed molecules. I_{ERS} and I_{Raman} are intensities in the enhanced Raman spectrum and normal Raman spectrum, respectively. Thus, the determination of the EF requires that the spectra from adsorbed and free molecules be measured under identical conditions.

To obtain a quantitative evaluation of the enhancement factor, Raman spectra of 4-Mpy surface-functionalized CdTe quantum dots and 4-Mpy solution are measured to obtain information on the band intensities of adsorbed and free molecules directly under the same conditions. Only with the concentration of 4-Mpy in aqueous solution above 0.2 M can signals of similar intensity be detected. Therefore, the ratio of Raman intensities between 4-Mpy surface-functionalized CdTe quantum dots and 0.2 M 4-Mpy solution is about 1.

Determination of the EF requires knowledge of the concentration of adsorbed molecules and the concentration of molecules in the solution effectively excited by the laser beam, namely, the number of molecules taking part in the scattering process. The concentration of adsorbed molecules was estimated by XPS data. Assuming all NaHTe has reacted, the concentration of CdTe in solution was 7.50×10^{-4} M. The concentration of Cd at the surface of CdTe quantum dots was calculated to be 1.95×10^{-4} M. Using the density of CdTe (6.06 g/cm^3), we can determine that each 3 nm dot contains about 210 molecules of CdTe, and of these some 55 are on the surface (see Supporting Information). Assuming each adsorbate molecule is attached to a Cd^{2+} atom (through the S) and using the ratio of the concentration of 4-Mpy to that of CdTe (about 1:18) from XPS, there should be about 3 adsorbed molecules per dot. Thus, the concentration of 4-Mpy adsorbed on CdTe quantum dots is calculated to be 1.08×10^{-5} M. Such a concentration of 4-Mpy molecules adsorbed on CdTe quantum dots is most likely overestimated due to the impossibility of completely reacting NaHTe, so we take this concentration to represent an upper limit. The concentration of 4-Mpy solution is 0.20 M. For the ratio of concentration, we calculate $[M_{\text{b}}]/[M_{\text{ads}}] = 1.85 \times 10^4$.

The Raman spectrum of 4-Mpy surface-functionalized CdTe quantum dots was compared to that of a 0.2 M 4-Mpy solution. Therefore, the EF was estimated to be 10^4 . It should be mentioned that the EF represents a lower limit since we determined an upper limit to the concentration of 4-Mpy molecules adsorbed on the quantum dot surface.

Enhancement Mechanism. The existing theory of enhancement in metals cannot be readily utilized to explain the above enhancement. It is generally accepted that there are two major contributions to enhancement in metals.³⁴ One is due to a large increase of the electric field caused by surface plasmon resonances induced by the laser light in nanosized metal clusters on the surface. This effect is usually considered the most important, contributing about 10^4 – 10^6 of the total observed enhancement (commonly described as around 10^6) and is often called the physical effect, since all that is required is that the molecules are physisorbed at or near the surface. In metals such as silver, the plasmon resonance is in the visible or near UV, making it suitable for enhancement of the Raman spectrum

excited in that region. For semiconductor quantum dots, the plasmon resonance is typically in the infrared. For CdTe quantum dots, we may determine the plasmon resonance frequency using the formula³⁵

$$\omega_{\text{p}} = \left(\frac{4\pi n e^2}{\epsilon_{\infty} m_e} \right)^{1/2}$$

where n is the electron carrier density, and m_e is the effective electron mass. Using $n = 1.7 \times 10^{18} \text{ cm}^{-3}$, $\epsilon_{\infty} = 7.2$, and $m_e = 0.11m_0$ ³⁶ (m_0 is the rest mass of the electron) we obtain a plasmon frequency of 2700 cm^{-1} . This value, which is typical of semiconductors, is too far in the infrared for the plasmon resonance to be responsible for the observed enhancement in CdTe.

The second factor contributing to the enhancement in metals is associated with chemisorption, and involves either molecule–metal or metal–molecule charge transfer. The most comprehensive theory³⁷ of this effect involves the application of Herzberg–Teller theory to the molecule–metal system, in which the vibronic levels are coupled due to a breakdown of the Born–Oppenheimer approximation. The initial step involves excitation of an electron from a filled orbital on the molecule to an empty level in the metal conduction band (or from a filled level of the conduction band to the lowest unoccupied orbital of the molecule).³⁸ It also provides an excellent fit to the observed resonance line shapes. This also explains why no Raman signal is observed from the coadsorbed 2-DMA since this molecule has no π^* -acceptor levels for charge transfer. However, applications of the charge-transfer theory usually can account only for about 10–100 of the observed enhancement factor. This is due to the rather broad ($>200 \text{ meV}$) homogeneous line widths (Γ) presumed in order to explain the excitation profiles observed. Note, however, that the charge-transfer (CT) contribution to the enhancement factor is proportional to Γ^{-4} (since, for a CT resonance the polarizability is proportional to Γ^{-2}). Thus if the homogeneous line widths are merely narrowed by a factor of 2 (say to 100 meV), the enhancement factor would be increased by an additional 2 orders of magnitude to 10^4 . In quantum-confined systems, where the diameter (3 nm in this experiment) is comparable to or less than the exciton Bohr radius³⁹ (6.8 nm in CdTe), quantum size effects narrow the width of the conduction band, making it resemble more the discrete levels of an atom. It is easy to see that somewhat narrower line widths might be achieved in confined quantum dots, resulting in considerable enhancement of the Raman signal.

There is clear evidence from our spectra that chemisorption is involved in the observed spectra. The 1113 cm^{-1} band is strongly enhanced, in comparison to the liquid. This band is due to a ring-breathing mode coupled to the C–S stretch. This indicates that the molecule is most likely attached to the quantum dot surface through the S adduct. Furthermore, the addition of 4-Mpy to the quantum dot has a strong influence on the emission spectrum (see Figure 4). This can only come about with strong interaction of the molecule with the quantum dot surface. Quenching of the emission of the quantum dots is also a byproduct of adhesion of the molecule to the surface. Convincing evidence for the CT mechanism can only come from identification of a CT transition in the appropriate region. This could be accomplished by observation of an absorption band, but such transitions are often broad and hard to detect. A more sensitive measure would be through a Raman excitation profile, and such experiments are currently being carried out in this laboratory. Note that in metal systems it was also possible to

prove the existence of CT contributions by electrochemical scanning of the applied potential (Fermi level) through the resonance,³⁸ but since for semiconductors the Fermi level is below the conduction band, this technique cannot be utilized in these systems.

Other evidence for the chemical enhancement mechanism is strongly associated with individual modes of the adsorbed molecules. Compared to those in the SERS spectrum on Ag colloid, there is greater enhancement of several bands, such as 1062, 1315, 1426, and 1476 cm^{-1} , relative to other bands in the SERS spectrum on CdTe quantum dots (Figure 3). For the 4-Mpy molecules adsorbed on the silver and CdTe nanoparticles, the predominant bands in the SERS spectrum (Figure 3) are located at 1585, 1113, and 1016 cm^{-1} , which have been assigned to the a_1 modes of the 4-Mpy molecules.^{40,41} Some weaker bands at 1476, 1426, 1315, and 1062 cm^{-1} were also observed. These bands have been assigned to the b_2 modes of the 4-Mpy molecules and can only be selectively enhanced by the CT mechanism through Herzberg–Teller contributions.^{42–44} The additional SERS enhancements from 4-Mpy–CdTe complex, in particular, the enhancement of the b_2 modes, obviously resulted from the formation of the 4-Mpy–CdTe molecular and could be ascribed to the charge transfer between the semiconductor nanoparticles and the 4-Mpy molecules.

Conclusions

We have observed an enhancement of the Raman signal from 4-mercaptopyridine adsorbed on CdTe quantum dots. The observed spectrum includes the CdTe LO phonon mode (at 167 cm^{-1}) as well as several Raman lines enhanced due to the proximity of the molecule to the quantum dot surface. Further observations include strong perturbation of the absorption spectrum of the quantum dots as well as suppression of the quantum dot photoluminescence due to the adsorbed molecule. The enhancement factor is estimated to be on the order of 10^4 . A charge-transfer mechanism is suggested as most likely responsible for the observed enhancement, since plasmon resonances are ruled out.

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Supporting Information Available: TEM images of mercaptopyridine surface-functionalized CdTe quantum dots. XPS data for the Cd, S, and N of mercaptopyridine surface-functionalized CdTe quantum dots. Raman shifts and assignments for 4-Mpy are shown in Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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