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Ambient Tip-Enhanced Two Photon Photoluminescence from CdSe/ZnS Quantum Dots

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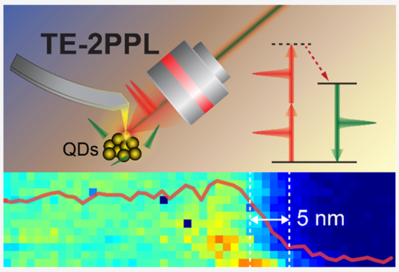
ABSTRACT: Nonlinear nano-optical measurements that combine ultrafast spectroscopy with tools of scanning probe microscopy are scarce. This is particularly the case when high spatial resolution on the order of a few nanometers is sought after in experiments performed under ambient laboratory conditions. In this work, we demonstrate the latter through measurements that track two-photon photoluminescence from aggregates of CdSe/ZnS quantum dots with sub-5 nm spatial resolution. Our proof-of-principle measurements that only take advantage of a plasmonic probe (as opposed to a gap mode) pave the way for nonlinear photoluminescence-based spectral nanoimaging of realistic/heterogeneous (bio) molecular and (bio) material systems.



■ INTRODUCTION

The combination of (non) linear optical spectroscopy and scanning probe microscopy led to significant advances in our understanding of (bio) molecular and (bio) material systems. Indeed, spatial resolutions far beyond the diffraction limit of light are attainable using nanospectroscopic techniques such as tip-enhanced Raman scattering (TERS)[1,2] and tip-enhanced photoluminescence (TEPL).[3] The significantly improved spatial resolutions in such measurements take advantage of the unique optical properties of metallic scanning probe tips.[4−6] Even though the highest demonstrated spatial resolutions required the stability of ultrahigh vacuum and ultralow temperature (UHV-ULT) setups,[1,2] pioneering measurements performed under ambient laboratory conditions[7,8] continue to be important and relevant, e.g., for (photo) catalysis and bioimaging applications.

As alluded to in the above overview, the vast majority of tip-enhanced nano-optical measurements utilize linear spectroscopies such as photoluminescence,[9] Raman,[7] and infrared[10] scattering. Using these approaches, single molecules were identified,[11] vibrational modes were visualized,[12] chemical transformations were tracked,[13,14] excitons in low dimensional quantum materials were characterized,[15,16] and Raman based all-optical sequencing was demonstrated.[17] All the latter was achieved with nanometer spatial resolution or better. Related nonlinear nano-optical measurements are relatively scarce, despite their promise and rich information content.[18] Early demonstrations of tip-enhanced nonlinear fluorescence[6] in fact preceded the first TERS report.[7] The pioneering nonlinear nano-optical measurements that targeted molecular fluorophores were however not revisited since the original report.[6] More recently, tip-enhanced coherent anti-Stokes Raman scattering[19] measurements were revived,[20] with a goal of characterizing a single virus. Our group has also contributed to this field through multimodal nonlinear nano-optical measurements that track localized optical fields in the tip-enhanced optical spectroscopy geometry.[21] That said, the number of reports that utilize nonlinear tip-enhanced optical nanoscopy to examine molecular and material systems is very small compared to more established linear nano-optical measurements.[16,18]

In this work, we revisit tip-enhanced nonlinear photoluminescence. We use a model system, namely, CdSe/ZnS quantum dots (QDs), which we have recently characterized using conventional (linear) ambient TEPL.[22] Akin to linear TEPL, tip-enhanced two-photon photoluminescence (TE2PL) is optimally enhanced when the plasmonic probe is in direct contact with the QDs. We match the previously documented TEPL resolution (<5 nm)[22] using our nonlinear excitation/photoluminescence scheme. We also rigorously demonstrate the reproducibility of our measurements through small area scans. We begin with an overview of our experimental methods.

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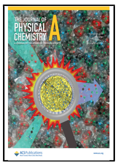

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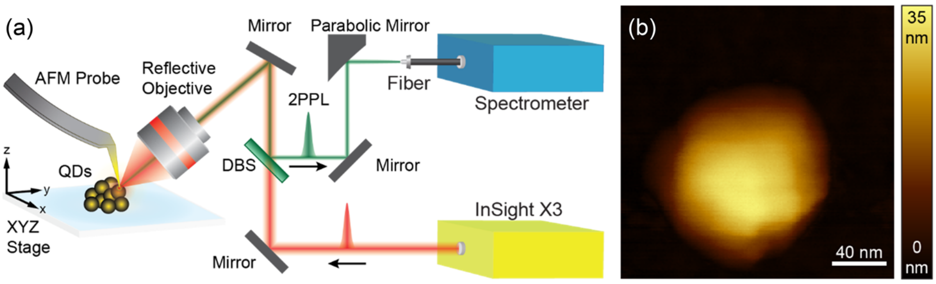

Figure 1. (a) Schematics of our TE2PL setup. The pulsed femtosecond 840 nm laser source (Spectra Physics, InSight X3) is focused onto an Au-coated AFM probe using an all-reflective objective (Thorlabs, LMM40X-P01). The scattered light that is nascent from a CdSe/ZnS aggregate is collected using the same objective, reflected off a dichroic beam splitter (DBS), and focused into a fiber-coupled detector (Shamrock SR-300i-Andor Newton DU970P-BVF EM-CCD) using a parabolic mirror. (b) Topographic AFM image of the CdSe/ZnS quantum dot aggregate that is analyzed in this work.

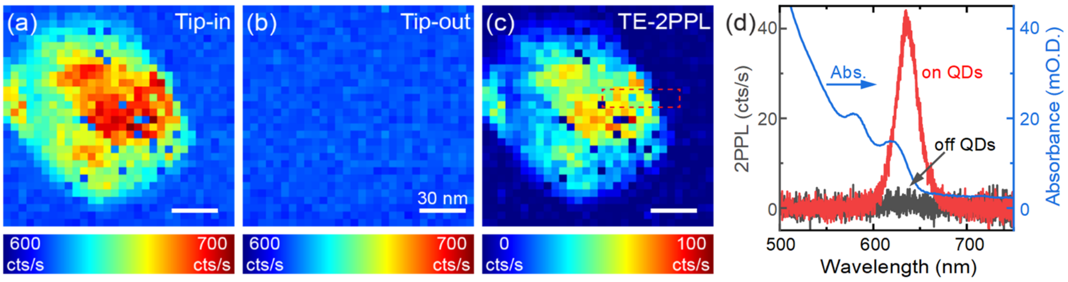

Figure 2. (a) Tip-in, (b) Tip-out, and (c) pure near-field TE2PL images of the area visualized in Figure 1b. The optical signals were spatially averaged in the 620−650 nm range for all three images, and the scale bar indicated 30 nm in all three panels. Note that tip-in spectral images are obtained when the tip is in direct contact with the sample, whereas tip-out signals were recorded when the tip and sample were separated by 10s of nm. (d) TE2PL spectra on/off CdSe/ZnS QDs are taken from panel (c), and they are shown along with the ensemble-averaged/bulk absorption spectrum in the same panel. Conditions: 0.5 mW average power, 0.5 s/pixel integration time, 5 nm lateral and vertical steps.

■ METHODS

Quantum Dot Sample. The CdSe/ZnS quantum dots were purchased from Oceannanotech (QSR-630−0010). Besides their narrow emission lines, we use the same quantum dots herein that we previously studied using TEPL[22] to enable a direct comparison between the observables in linear and nonlinear nano-PL. The stock solution was diluted 100 times in toluene, and otherwise used without further modification. The optical density of the diluted solution was measured in a quartz cuvette using a commercial UV−vis instrument (Horiba, Duetta).

TE2PL Measurements. The TE2PL sample was prepared by drop-casting a 15 μL solution of the diluted QD solution (see above) on a silicon chip. After the solution was air-dried, the substrate was rinsed with excess amounts of acetone. The experimental setup is schematically illustrated in Figure 1. It is based on a previously described AFM-optical platform.[18] For the purpose of this work, the driving laser consists of an 840 nm/80 MHz source that is attenuated to ∼0.5 mW (average power) at the sample position. The exact conditions used for each TE2PL image reported here are otherwise given in figure captions. Atomic force microscope (AFM) tips were prepared by sputter coating commercial silicon probes (Nanosensors, ATEC-NC) with 100 nm of gold. The typical oscillation amplitudes of the probes are in the 20−40 nm range and their resonance frequencies are ∼250 kHz. Whereas AFM maps were recorded in tapping mode, TE2PL spectra employed a hybrid AFM feedback operation. Namely, two spectra were recorded at every tip position: "tip-in" signals when the tip is in direct contact with the sample, and "tip-out" spectra when the tip was retracted by 20−40 nm. Sample motion was otherwise still accomplished using a tapping mode feedback loop in the nano-optical measurements to minimize tip-induced perturbations to the QD assemblies probed.

■ RESULTS AND DISCUSSION

Figure 1a schematically illustrates our TE2PL setup. The driving laser source consists of a single high repetition rate femtosecond laser source, which is steered and focused onto the apex of a gold-coated AFM probe using an infinity corrected all-reflective objective. The polarization of the incident laser is set to coincide with the long axis of the tip. Nanopositioning of the incident laser source is achieved using an xyz piezo objective scanner (not shown in the schematic). The scattered linear and nonlinear optical radiation is collected through the same objective, reflected off a short pass dichroic beam splitter, and directed onto the detector. Figure 1b shows a nanoisland that is comprised of an aggregate of QDs. Our ensuing TE2PL measurements and their analyses are focused on this area of the substrate.

Our near-field images were recorded using intermittent contact AFM feedback. Namely, two different optical signals were recorded at every position of the tip relative to the sample. The first signals result in the image shown in Figure 2a. These signals are obtained when the tip is in direct contact with the substrate. The second set of signals, recorded when the tip is ∼30 nm away from the sample, together comprise the image shown in Figure 2b. Note that the entire area (tip, sample area shown in Figure 2) is irradiated in both cases. Under our experimental conditions (laser power and integration time), the tip-out spectra (Figure 2b) are dim (also see Figure S1). Still, we strictly define the pure near-field image as the difference between the tip-in (Figure 2a) and tip-out (Figure 2b) spectral images. The background-subtracted near-field image is shown in Figure 2c. Inspection of all three images and representative tip on-QD and tip off-QD spectra (Figure 2d) reveals the sharp optical contrast obtained when the tip is in contact with the QDs. This is reminiscent of the linear TEPL spectral nanoimages of the same type of QDs.[22] It appears that enhanced two-photon absorption and plasmonic field enhancement dominate the TE2PL signals, much like in TEPL.[9,22] This picture is also consistent with a recent study by Yang et al. In their work, subnanometer resolution and optimal signal enhancement in UHV-ULT TEPL measurements were obtained when the tip was in contact with an isolated molecule.[3]

Figure 3 shows a high resolution pure-near field TE2PL map of the small area toward the edge of the QD aggregate, which is highlighted used a red rectangle in Figure 2c. Fine lateral/vertical step sizes of 1 nm were used here to gauge the attainable spatial resolution of our measurements. The nearly symmetric nature of the edge visualized in Figure 3a ensures the reproducibility of our measurements as the horizontal cross sections are sequentially stacked from the bottom to the top of the image. Several aspects of the topographic and optical cross-sectional line profiles shown in Figure 3b are worth highlighting. First, the optical resolution is clearly superior to its topographic analogue. This is because the first is governed by optical field nanolocalization, whereas the second is limited by the nominal probe radius. For the sputtered probes used in this work, our observations of <5 nm spatial resolution in prior linear TEPL[22] and current TE2PL (Figure 3b) measurements are attributed to a combination of field enhancement and the so-called lightning rod effect. The latter is because our probes sustain corrugations that lead to further field localization, as discussed elsewhere.[23] In this aspect too, our observations are consistent with the analysis of Yang et al, where an atomically decorated plasmonic probe was used to further enhance UHV-ULT TEPL measurements. Overall, the TE2PL spectra we observe here are reminiscent of their linear TEPL analogues in many ways. This is clear in the spectral analysis of the high-resolution map in Figure S2. Note that we again observe Stark-induced exciton resonance variations (red-shifts mainly), as discussed in our previous TEPL work.[22]

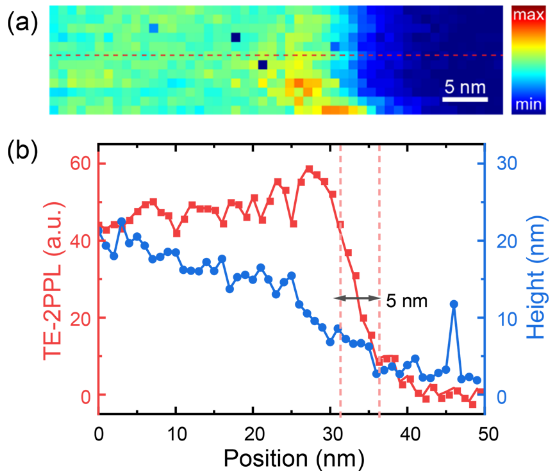

Figure 3. (a) High resolution pure near-field (tip-out subtracted) TE2PL map of the dashed red rectangular area toward the edge of the QD aggregate (see Figure 2c). The image shown is integrated in the 620−650 nm range. (b) TE2PL (red) and AFM (blue) cross-sectional cuts measured along the dashed red line shown in panel (a). Conditions: 0.5 mW average power, 0.5 s/pixel integration time, 1 nm lateral and vertical steps.

The pioneering work of Sánchez et al., which was performed more than 20 years ago, demonstrated ∼20 nm spatial resolution in tip-enhanced two-photon fluorescence from proteins.[6] Interestingly, and with the goal of minimizing fluorescence quenching from the metallic probe, the authors maintained a 2 nm gap between the tip and sample.[6] Through careful nanocavity control, including tip-apex engineering with an atomistic protrusion and subnanometer positioning precision in UHV-ULT TEPL measurements, Yang et al's observations were distinct.[3] Namely, the more recent study found that the optical signals are optimally enhanced when the tip is in contact with the molecule. This is consistent with our present observations, recent TEPL literature more generally,[9] and a tip-enhanced second harmonic generation study that targeted extended 2D excitonic systems.[16] In terms of spatial resolution, the recent UHV-ULT work together with the attainable spatial resolutions demonstrated both here and in our recent TEPL study[22] altogether suggest that the only limits to the attainable spatial resolution have to do with (i) the size of the protrusion (if any) at the tip apex, and (ii) the stability (or lack of) of scanners under UHV-ULT vs. ambient laboratory conditions. Evidently, the AFM feedback used in our vs the previous[6] TE2PL work also affects the attainable spatial resolution. Naturally, tip modification under intense femtosecond irradiation throughout the course of the measurement is an important consideration to keep in mind.[16]

■ CONCLUSION

In conclusion, this work demonstrates the feasibility of ambient TE2PL with <5 nm spatial resolution under ambient laboratory conditions. Our observations and analysis extend our recent high spatial resolution ambient TEPL measurements[15,22] to the nonlinear TE2PL realm. There are several advantages to nonlinear excitation/emission in the TE2PL scheme, including the possibilities of visualizing dark excitons and engineering/controlling nonlinear light−matter interactions on the nanoscale. Consistent signal levels and redundant scan/rescan-type measurements (Figure 3) ensured the reproducibility of our observations. Overall, we found that TE2PL signals are optimally enhanced when the tip is in contact with the substrate, which is similar to what is known for TEPL of excitonic material systems. Further measurements are however needed to better examine the operative nanoscale selection rules in TE2PL. This will be the subject of future reports.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.2c07750.

Tip-in vs tip-out spectra on and off the QD aggregate and a combined topographic-spectral analysis of the high-resolution image shown in Figure 3 (PDF)

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Notes

The authors declare no competing financial interest.

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