Surface-enhanced Raman spectroscopy of CdSe quantum dots on nanostructured plasmonic surfaces

James T. Hugall, Jeremy J. Baumberg, and Sumeet Mahajan[a]

NanoPhotonics Centre, Cavendish Laboratory, University of Cambridge, Cambridge CB3 OHE, United Kingdom

Although quantum dots (QDs) are widely used as fluorophores they have not so far been used as Raman labels. Here we demonstrate (resonant) surface-enhanced Raman scattering (SERS) of CdSe QDs attached to nanostructured plasmonic surfaces. The 208 cm^{-1} CdSe longitudinal optical phonon mode is observed for laser excitation at 514, 633, and 785 nm. Tuning the SERS signal into resonance with the localized surface plasmon reveals the effects of optical absorption and emission on QD SERS. Equivalent tuning of the localized plasmons on graded nanovoid samples shows strong resonant SERS enhancements. These results pave the way for exploiting QDs as SERS markers. © 2009 American Institute of Physics. [doi:10.1063/1.3243982]

Semiconductor quantum dots (QDs) are of interest for many applications due to their narrow photoluminescence (PL) lines, high quantum yield, and broadband absorption spectra.[1,2] Most sensing and imaging applications currently use PL[2,3] due to its greater sensitivity compared with other spectroscopic techniques such as Raman scattering. For PL, QDs possess many attractive features over standard molecular dye markers including their broad excitation region, resistance to photobleaching, low photo- and chemical degradation, and size-tunability of their narrow emission peak.[3] Although the use of QDs as fluorophore labels has been well studied,[4] their use as Raman labels has yet to be realized.

Because of its small cross-section ($\sim 10^{-29}$ cm^2 molecule^{-1}), Raman scattering is inherently weaker than fluorescence ($\sim 10^{-16}$ cm^2 molecule^{-1}).[5] However in surface-enhanced Raman scattering (SERS), plasmonic surfaces enhance the Raman scattered light from molecules on or near the surface by 10^6 to 10^{12} times.[6] Moreover in surface-enhanced resonance Raman scattering (SERRS), the enhancements can be further increased by several orders of magnitude when exciting at an electronic resonance of the chromophore.[7] Thus SE(R)RS (SERS or SERRS) can be more sensitive than fluorescence with the added advantage of detection specificity and multiplexability.[8] These enhancements are due to the intense local electric fields caused by exciting surface plasmons at metal surfaces.[9] It is now possible to design nanostructured gold surfaces to provide tuned SERS substrates with good enhancement reproducibility.[7,10–13]

Besides QDs acting as (bio)chemical markers, the ability to detect (sub)monolayer concentrations of QDs through SERS can be useful for monitoring QD devices in real time, for instance measuring the QD temperature or tunnelling-induced phonon emission in photovoltaic or QD LED devices. Here, we show SE(R)RS of CdSe QDs on nanostructured gold surfaces.

CdSe/ZnS core/shell QDs with 6 nm diameter and an emission peak at 640 nm were attached to nanostructured gold surfaces. Two well-characterized plasmonic substrates were used: a commercially-available square array of micron-sized inverted pyramids [Klarite™,[10] Fig. 1(a)] and graded nanovoids[14] comprised of hexagonal arrays of truncated spherical voids of controllable thickness [Fig. 3(a)]. The QDs (Nanoco Technologies) are capped with hexadecylamine (HDA) and trioctylphosphine oxide which act as binding and stabilizing agents. Using standard thiol chemistry,[15] a self-assembled monolayer of 3-mercaptopropionic acid (MPA) was adsorbed on the gold surfaces. The thiol displaces other species adsorbed on the surfaces and ensures submonolayer coverage due to only weak hydrophobic interactions with the QDs. The modified surfaces were then placed overnight in a 1 mg/ml solution of QDs in toluene to allow them to bind to the surface, before rinsing to remove excess QDs. Using AFM we quantify the coverage as $\sim$450 QDs/μm^2. Both the Klarite nanostructures and "flat" gold (which has nano-
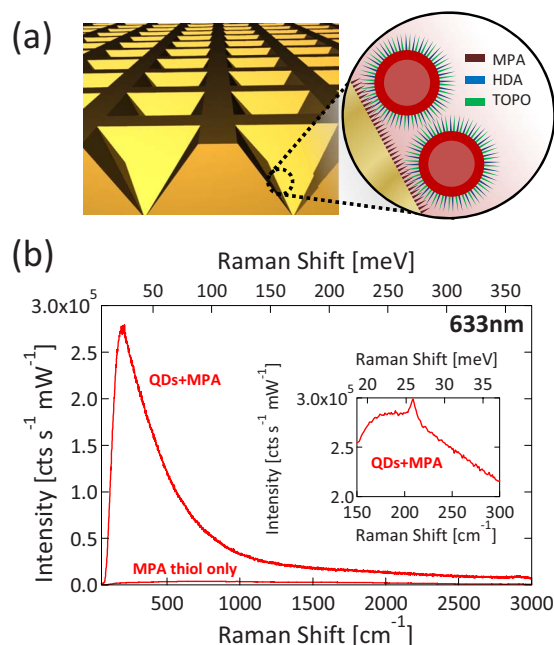

FIG. 1. (Color online) (a) Thiol-attached QDs on an array of gold-coated inverted pyramids. (b) SE(R)RS of the surface with MPA thiol only and after attachment of QDs. Inset shows SERRS peak at 208 cm^{-1}.

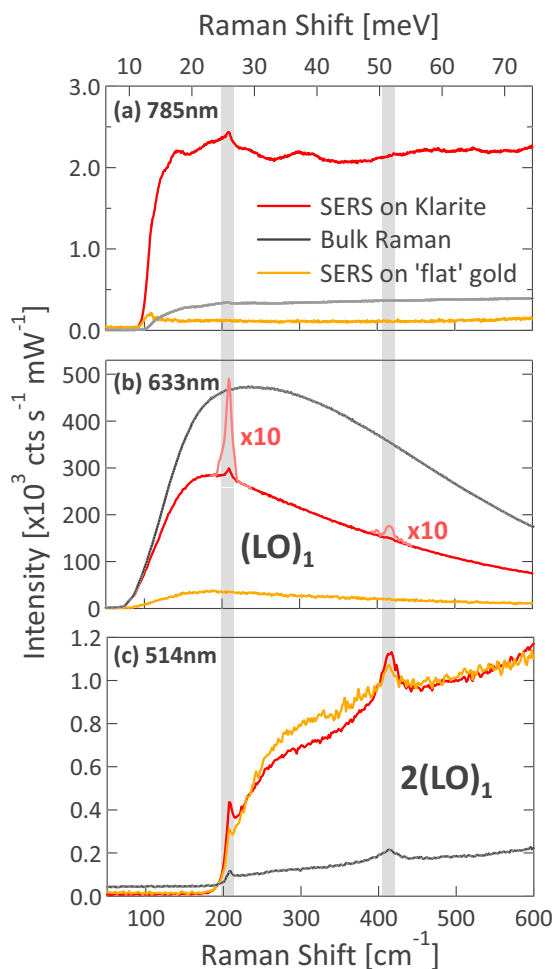[a]Electronic mail: sm735@cam.ac.uk.

FIG. 2. (Color online) QD SERS spectra of Klarite and flat gold, using laser excitation wavelengths (a) off resonance at 785 nm, (b) on emission resonance at 633 nm, and (c) within absorption at 514 nm. Raman spectra of bulk aggregated QDs are also shown. The peak at 35 meV in (a) comes from the MPA (Ref. 19).

scale roughness caused by the deposition process) were used to record SERS spectra. Raman spectra of bulk QDs were acquired for comparison by drying a concentrated (50 mg/ml) solution into an opaque agglomerate. Measurements were taken at three wavelengths: 785, 633, and 514 nm, allowing comparison of SERS on and off resonance with the QD absorption and emission.

Successful attachment of QDs to Klarite is confirmed by the large background on the SERRS signal arising from the tail of 640 nm PL emitted by resonantly excited QDs [Fig. 1(b)]. The QD phonon is more clearly seen in the inset SERRS spectrum, superimposed on this PL.

The QD SERS spectra on Klarite nanostructures and on flat gold, with the corresponding Raman of bulk aggregated QDs, are shown in Fig. 2. On Klarite at all three laser wavelengths, a SERS peak at 208 cm^{-1} is present. This peak corresponds to the longitudinal optical phonon mode $(LO)_1$ of CdSe.[16–18] Also observed is the two-phonon mode, $2(LO)_1$. The SERS enhancement of these phonon modes varies strongly with the laser excitation wavelength, being >100 stronger at 633 nm [note y-scale in Figs. 2(a)–2(c)].

At 785 nm [Fig. 2(a)], the SERS on Klarite displays more peaks than at other laser wavelengths. In the low frequency region shown, although the principal CdSe $(LO)_1$ mode dominates, many other peaks are present corresponding to SERS of HDA, MPA and other adsorbed species.[19] No SERS is seen on flat gold as expected from the absence of localized plasmon modes. At this wavelength, Raman of the bulk QDs (with >10^3 times more QDs in the laser spot) shows a weak CdSe $(LO)_1$ peak, while other peaks are absent. The Klarite surface used here is designed to have resonances near both 785 and 633 nm using the techniques discussed in Ref. 10. Consequently SERS at 785 nm is enhanced by the substrate enabling observation of QD phonon modes as well as molecular vibrations from molecules adsorbed both on the QDs and on Klarite.

At 633 nm [Fig. 2(b)], the laser is in resonance with the QD absorption *and* emission as well as the localized plasmon. An intense background from PL of the QDs is observed which dwarfs most of the Raman peaks seen at 785 nm. While Raman of bulk QDs and SERRS on flat gold show no peaks, the QD SERRS signal on Klarite shows a strong $(LO)_1$ peak and the corresponding $2(LO)_1$ harmonic. We see no evidence of the ZnS LO phonon. The combined electronic and plasmonic enhancement yields peak amplitudes which are 200 times that at 785 nm, hence QD SERRS is >10^2 times the SERS signal.

At 514 nm [Fig. 2(c)], the laser is no longer in resonance with QD emission. Despite this the $(LO)_1$ peak is clearly visible in the SERS spectra on Klarite (although prematurely cutoff by the Raman notch filter) and has a peak amplitude a third of that using 785 nm excitation. The $2(LO)_1$ harmonic is now observed very strongly [with amplitude double the $(LO)_1$ phonon line]. In distinct contrast to the other wavelengths, these results are similarly found for the SERS on flat gold and the bulk QD Raman signal. Light at 514 nm is absorbed directly within the QD and so ingoing and outgoing resonant Raman scattering (RRS) is responsible for the large bulk QD Raman signals observed. This RRS dwarfs the peaks from other adsorbed species (similar to SERRS at 633 nm). The absence of any localized plasmon resonance on Klarite at this wavelength explains the similarity between the SERS signals on Klarite and flat gold. We believe the SERS enhancement at 514 nm is caused by the excitation of propagating SPPs from weak random roughness of the surface—at 514 nm these SPPs will be more closely confined to the surface than at longer λ, thus generating stronger plasmon fields.

These data demonstrate the SE(R)RS of QDs and its tunability with excitation wavelength. To demonstrate the dependence of QD SERRS on plasmonic resonances we utilize a graded nanovoid sample [Fig. 3(a)]. Nanovoids are fabricated by electroplating through a monolayer of self-assembled spheres, which are subsequently removed to give an array of interconnected voids. By retracting the template from the electrodeposition solution at various intervals, different thicknesses can be deposited on the same sample resulting in a graded substrate.[14] Plasmons on nanovoid surfaces are well characterized and tune with the void depth.[12,20] A graded gold nanovoid substrate templated with 600 nm diameter spheres, which possesses plasmon resonances around 2 eV, was fully mapped using reflectance measurements on an angle-resolved goniometer [Fig. 3(b)]. After QDs were attached to the surface, SERRS measurements were carried out using 633 nm laser excitation, at regular spaced intervals across the sample (corresponding to different normalized thicknesses). This allows comparison of the
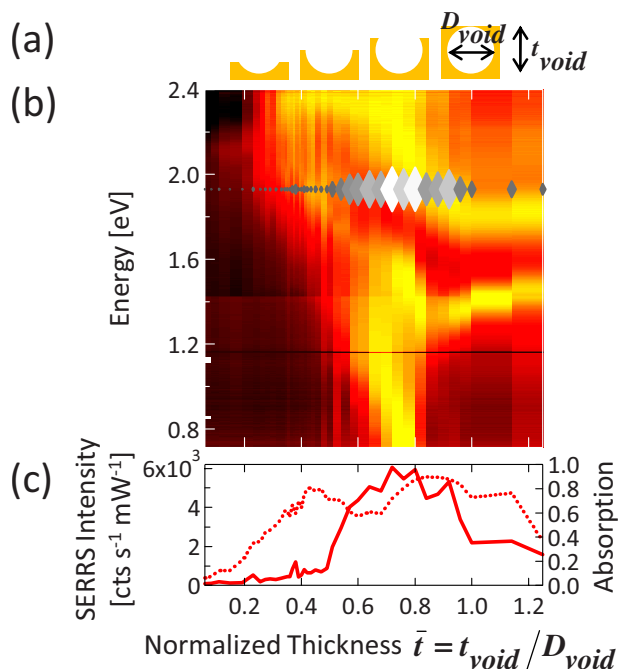
FIG. 3. (Color online) (a) Nanovoid geometry vs thickness. (b) Image: Reflectance vs thickness (normalized to the void diameter) for graded nanovoid sample, yellow indicates low reflectivity (plasmon resonant absorption). Image overlaid with SERRS amplitude (as marker size) of the CdSe $(LO)_1$ mode excited at 633 nm. (c) Sample absorption (dashed) at the Stokes Raman energy (1.93 eV) and SERRS amplitude (line), vs normalized thickness.

plasmon resonances with the SERRS enhancement.

The background-subtracted peak height of the CdSe $(LO)_1$ mode is plotted over the reflectivity data [Fig. 3] revealing how the SERS enhancement of the $(LO)_1$ mode increases as it comes into resonance with the localized plasmon modes of the void. This proves the importance of localized plasmons for SERRS enhancements and supports earlier results for molecular SE(R)RS on nanovoids.[7,12]

These results demonstrate that SE(R)RS is an appropriate tool to directly measure phonon excitations in QDs, giving signals of $\sim$1 photon QD^{-1} s^{-1} mW^{-1} which can be further optimised. Phonons in CdSe/ZnS QDs are clearly observed at three different wavelengths which give different enhancements due to the relative tuning of emission, absorp-

tion, and plasmonic spectra on two different plasmon-enhanced gold nanostructured surfaces. This study paves the way for use of QDs as SE(R)RS markers as well as to study QD electronic devices.

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