Luminescence Studies of Individual Quantum Dot Photocatalysts

Lilac Amirav and A. Paul Alivisatos

Department of Chemistry, University of California at Berkeley, and Materials Science Division,
Lawrence Berkeley National Laboratory, Berkeley, California 94720

Supporting Information

1. Synthesis of Pt tipped CdSe/CdS rods photocatalysts

1.1 Synthesis of CdSe seeds:

The procedure for synthesis of CdSe seeds was adopted from Manna and coauthors *(4)*. 3.0 g of trioctylphosphine oxide (TOPO), 0.280 g of cctadecylphosphonic acid (ODPA), and 60 mg of cadmium oxide (CdO) were mixed in a 25 mL three-neck flask, heated to 150°C, and subject to vacuum for 1 h. The solution was then heated to 300°C under argon, until it turned optically clear and colorless, to dissolve the CdO. At this point, 1.5 g of trioctylphosphine (TOP) was injected into the flask. The temperature was raised to 370°C and a TOP:Se solution (0.058 g Se + 0.360 g TOP) was injected. The reaction time was modified to obtain CdSe dots of different sizes. 2.3-nm CdSe seeds were obtained by removal of the heat immediately after the injection, while the 3.9 nm CdSe seeds were obtained by stopping the reaction after 5 minutes. After the synthesis, the nanocrystals were cleaned of excess reactants and surfactants by repeated cycles of precipitation in methanol and washing by re-dissolution in toluene. The CdSe seed diameter was calculated from the position of the peak maximum of the first exciton absorbance. *(SR1)*
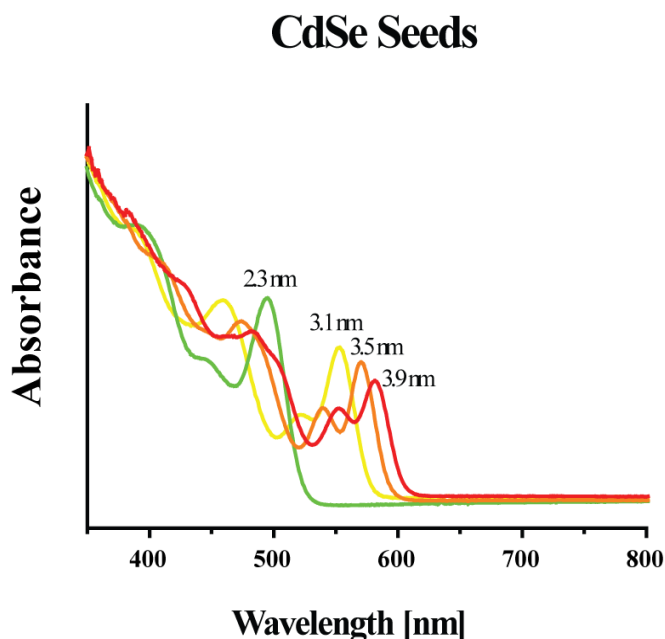
CdSe Seeds

Fig. S1. CdSe seeds synthesized with different size: 2.3 nm, 3.1 nm, 3.5 nm, and 3.9 nm.

1.2   Synthesis of CdSe/CdS nanorods:

The procedure for the seeded rods synthesis was adopted from Talapin et al. *(5)* 0.207 g of CdO, 1.08 g of ODPA, 0.015 g of propylphosphonic acid, and 3.35 g of TOPO were loaded into a 25mL three-neck flask and heated to 120°C for 30 min under vacuum. The mixture was heated to 320°C under flowing argon to produce an optically clear solution. After the CdO completely dissolved, the solution was cooled to 120°C and put under vacuum for 2 h for the removal of water, after which it was heated to 340°C under flowing Ar. At this time, 1.5 g of TOP was injected and the flask was allowed to return to 340°C. TOP:S was prepared by reacting equimolar amounts of TOP and elemental sulfur under an inert atmosphere. 0.65 g TOP:S was injected into the flask at 340°C, followed by the injection of the CdSe seeds dissolved in 0.50 g of TOP after 20 s. The reaction temperature was adjusted to 320°C, and the reaction was stopped after 10 min by the removal of heat and the injection of 4 mL of anhydrous toluene. The nanorods were isolated and cleaned by a few cycles of precipitation with isopropanol/acetone as non-solvent (10:7 relative to solvent) and re-dissolution in toluene/hexane/chloroform, with alternating addition of 1-2 ml of octylamine and nonanoic acid. Precipitation was achieved by centrifugation at 4000 rpm for 20-30 min. Modifications to this synthetic procedure allowed for the control of nanorod length and diameter. The length of the rods could be controlled by the injection of different amounts of CdSe dots such that more dots result in shorter rods. We used this approach for the synthesis in this work, since this variation leaves the rod diameter relatively unaffected (~4 nm). In order to obtain similar length of about 40 nm with the different seed sizes, we injected about 40 nmol of 3.9-nm seeds (0.49 g of seed solution in toluene with a seed concentration of 7.7 x 10^{-4} M), and 60 nmol of 2.3-nm seeds (0.36 g of seed solution in toluene with a concentration of 1.5 x 10^{-4} M). Also, the reaction time could be used to control rod length; longer growth times produce longer rods. In addition, the diameter and length of the rods could be controlled by the amount of TOP:S injected into the reaction; more TOP:S produces longer and thinner rods.

1.3 Synthesis of Pt Tips on the CdSe/CdS Nanorods

The procedure for Pt tipping was adopted from Habas SE et al. *(7)*. Oleic acid (0.2 mL), oleylamine (0.2 mL), 43.0 mg of 1,2-hexadecanediol and 10 ml of diphenyl ether were loaded into a 25 mL three-neck flask and heated to 80°C under vacuum for 30 min to remove traces of water. Pt acetylacetonate (~20 mg) was added to a suspension of CdSe/CdS rods (about half of the synthesis product) in dichlorobenzene (~1 ml) and the solution was soniceted for a few seconds to promote dissolution of the Pt precursor. Under argon, the mixture of surfactants and diphenyl ether was heated to 200ºC. At this point the Pt precursor and seeded rods in dichlorobenzene were injecting into the flask. Upon temperature recovery to 200 ºC the solution turned black. After several minutes (about 4 min; the time depends on the amount of seeded rods and the quality of their cleaning procedure) the reaction was removed from the heating mantle and quenched in a water bath. The Pt tipped nanorods were isolated and cleaned by a few repeatable steps of precipitation/redissolution. Homogenous nucleation of Pt dots in the reaction flask contributed to the strong black colure of the crude product. The clean solution of Pt tipped seeded rods in toluene is brown.
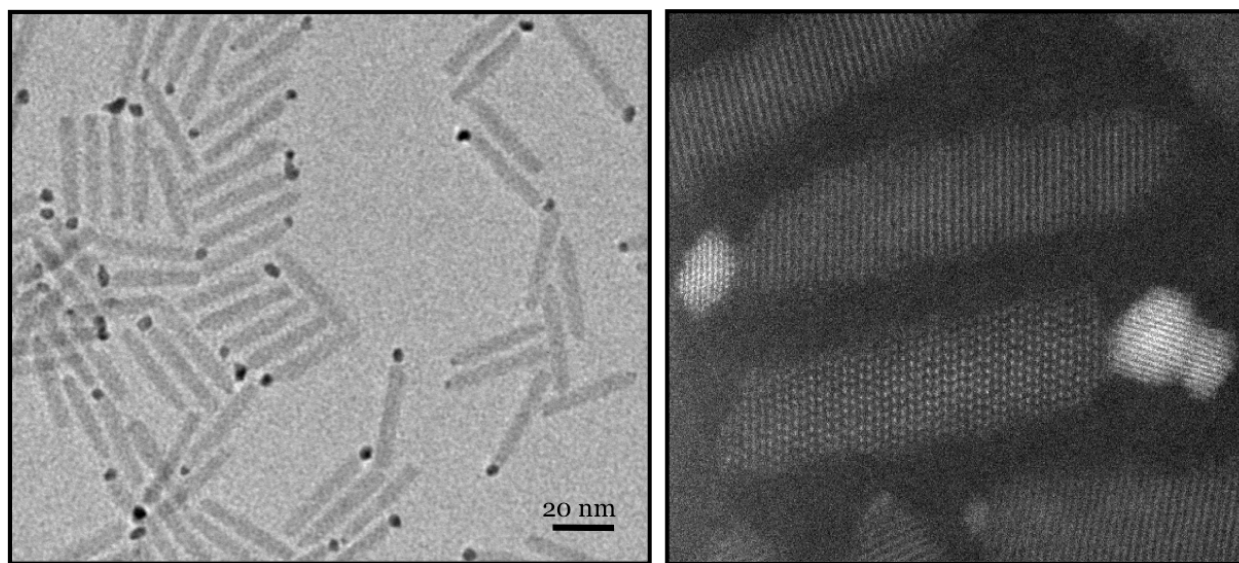

Fig. S2. *On the left, TEM of one of the examined samples, demonstrating the relatively good synthetic control over the rods length distribution. One the right, HAADF (taken by Quentin Ramasse, NCEM) demonstrating the wide heterogeneity with respect to the Pt tip size, shape and interface with the CdS rod.*

2. Experimental Apparatus

In this research we used far-field optical microscopy to explore the fluence-dependent particle photoluminescence. While the actual particle cannot be imaged by this technique, as it is smaller than the diffraction limit of visible light, the light emitted from individual nanocrystals is sufficiently localized such that the position of the nanocrystal can be determined and the emitted light can be analyzed (the sample concentration was adjusted for single particle measurements). The sample was spin casted at low concentration on a substrate, typically quartz cover slide, and placed in a gas tight cell under Ar (at atmospheric pressure). The sample was illuminated with a Lexel Ar Ion Laser (Model 95) at a wavelength of 457.9 nm, using a set of ND's to modify the excitation light intensity. The laser beam was directed through appropriate laser line filter and lenses, before it entered a Zeiss Axio-observer Z1 inverted microscope where it was focused onto the sample by a long working distance objective (Zeiss 50x NA=0.55, WD=9 mm). The laser beam diameter was measured via projection thought a TEM grid. The photon flux was calculated using the laser beam measured intensity, divided by the illuminated area, and multiplied by the average particles absorption cross section.

The photoluminescence signal from the sample was directed through Acton Spectrometer (equipped a mirror), onto a Princeton Instruments liquid nitrogen cooled CCD (Spec-10:400B) with a 1340 by 400 chip.

Perhaps the most significant merit of a single particle measurement is our ability to elucidate inimitable characteristics, which could later be correlated to geometrical properties of the photocatalyst. We preformed preliminary direct correlation between the fluorescence optical microscopy and electron microscopy, verifying that the fluorescent sample is tipped with Pt. This correlation is based on the possibility to identify and determine the position of the fluorescent structure directly on the TEM grid by means of fluorescence microscopy, and the recovery of these positions during subsequent investigations with TEM. The absolute coordinates of the area of interest on the grid can be determined by microscopy (three corners of the grid window or other markers) and recovered in the electron microscope (as seen in Fig. S3). This technique offers an exceptional opportunity for more systematic research correlating structural and chemical reactivity with properties of the individual photocatalyst in question.
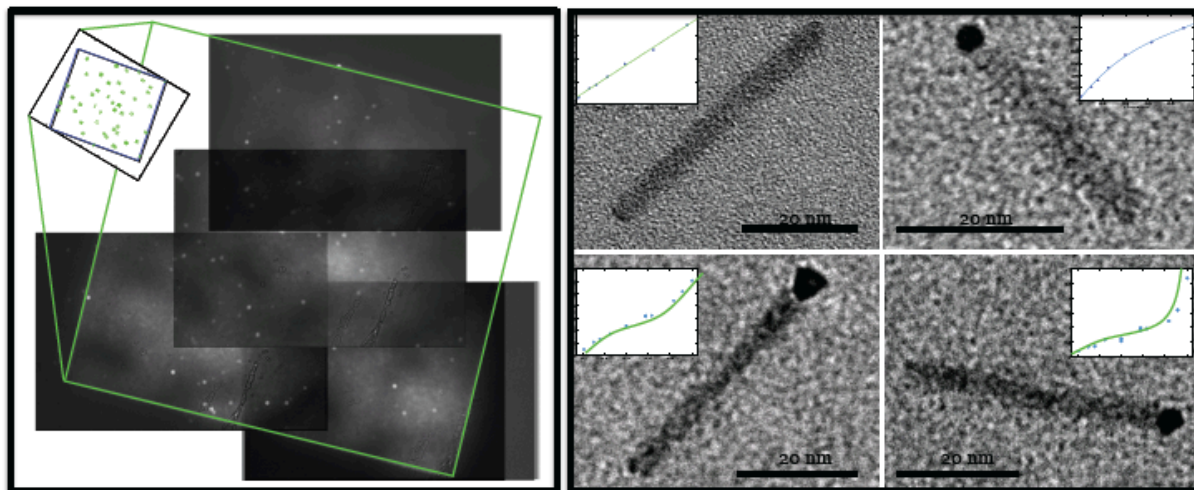
Fig. S3. On the left, demonstration of a reconstruction of a particular area composed of a few different examined sites under the optical microscope. In green are the borders of the TEM grid window. Each particle is identified via three coordinated using the window corners. On the right, a few examples of particles identified with TEM and in the insert, their corresponding fluence-dependent spectra.

We examined the fluence-dependent spectra by increasing and decreasing the laser power, to confirm that the observed increase of the photoluminescence at high photon fluxes is not merely a result of some damage to the rod (e.g. loosing its Pt tip). No hysteresis was observed.

3. Data Analysis

About 97% of the rods examined demonstrated the same trends. Figure S4 portrays a mini gallery of fluence-dependence data obtained from few individual rods measured under Ar, to give the readers a taste of the variations observed from one sample to another. Although the trends were similar, the saturation onset altered from one sample to the next.
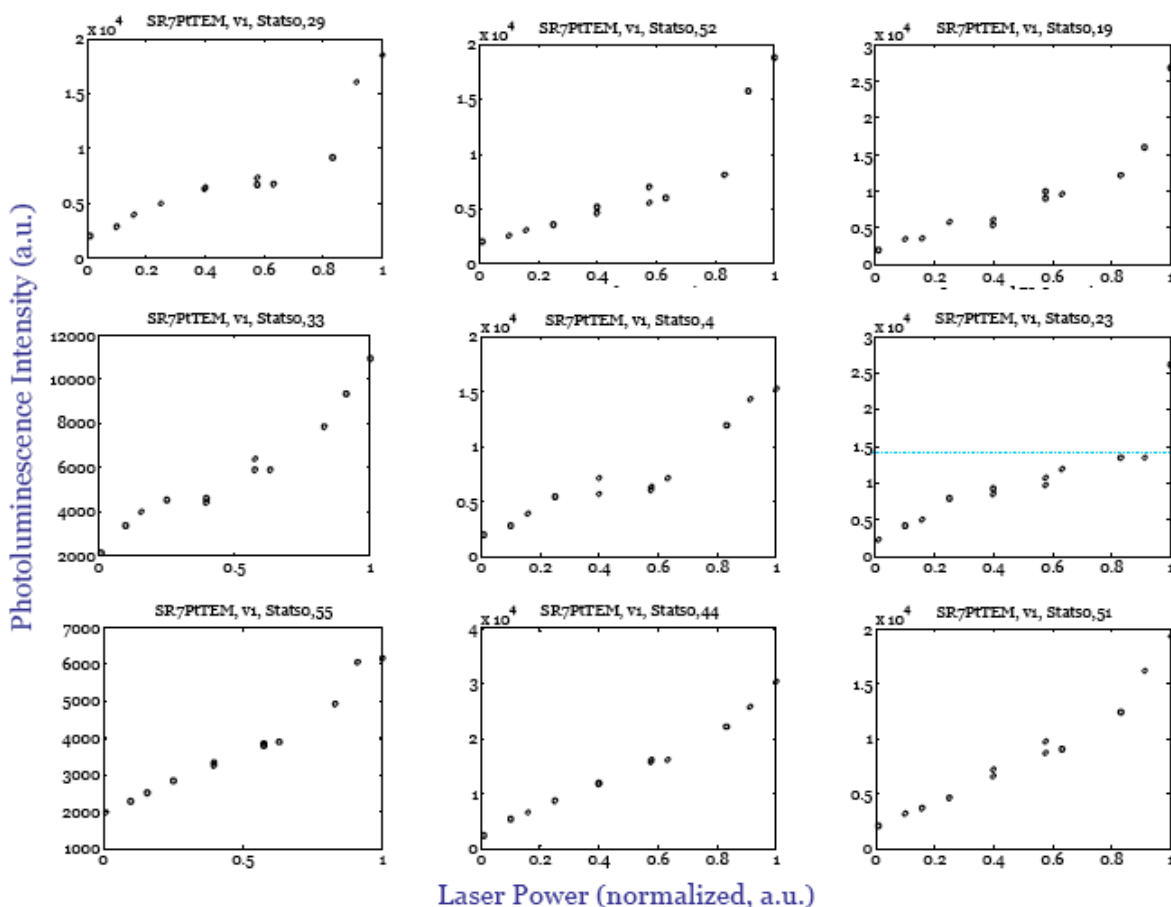

Fig. S4. A mini gallery portraying fluence-dependence data obtained from a few individual particles.

The single particle measurements have played an essential role in disentangling the observed deflections from linearity of the power dependence of the photoluminescence. An extreme example is presented in Figure S5, which shows opposing trends obtained from two individual particles from the same sample (3.9 nm seed embedded in a 60 nm long rod).
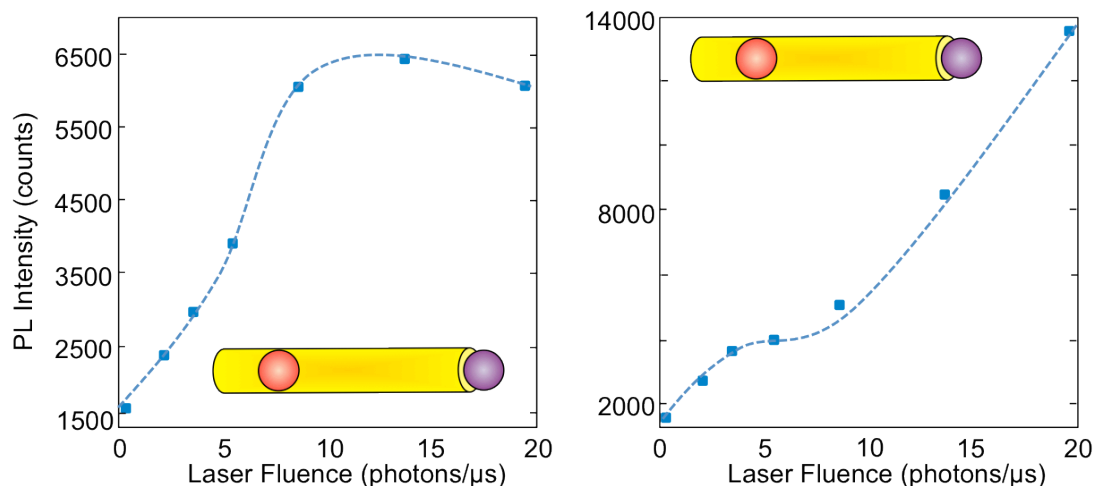
Fig. S5. Fluence-dependence obtained from two individual particles from the same sample.

Analysis on the single particle level allowed for de-convoluting of fluorescence intermittency (SR2), which is also known to be fluence dependent. This was resolved experimentally by analyzing data only from the "on" state of the particle, a method that is exclusively suitable for single particle analysis. Using MATLAB we integrated a fixed area around the image of each individual particle as recorded on the CCD, and subtracted the local background reading (similar to the orange square in the insert in Fig. S6). For every photon flux we have recorded a set of 30 images with integration time of 1 sec. Fig. S6 presents an example of such set for a few particles at one photo flux. Blinking can be easily identified, providing evidence that we are observing single particles. The maximal reading was chosen as the data point of the fluorescence intensity. Averaging the reading from these 30 images is equivalent to a 30 sec integration time.

Thermal effects were also accounted for. We have examined the samples spectra with increasing temperature. Noticeable spectral changes were observed. As we did not observe spectral changes with fluence, we concluded that there was no significant raise in temperature.
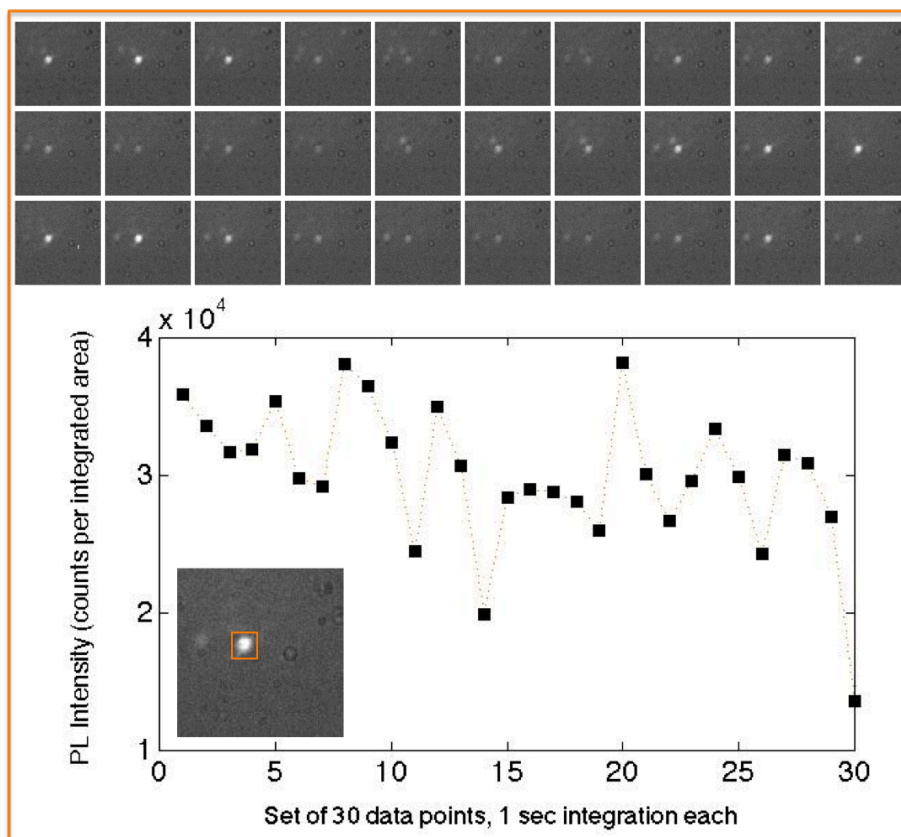
Fig. S6. De-convoluting of fluorescence intermittency with MATLAB analysis on the single particle level. Top: A set 30 images for a few particles, as recorded on the CCD, at one photo flux (integration time of 1 sec). Bottom: The integrated PL intensity from a fixed area around the image of one individual particle (orange insert) is plotted.

The charge separated state lifetimes were estimated from the saturation onset. This was very roughly determined by the intersection of two linear lines drown upon the two different slops of the different sections of the PL trends. Under Ar, this saturation onset was typically found to occur at 5-9 photons/μs, corresponding to a charge-separated state lifetime of 100-200 ns. In water the saturation onset was around 8 photons/μs, and thus we estimated the charge-separated state lifetime to be 120 ns. In a similar way we estimated the charge-separated state lifetime to be 250 ns in water plus 10% methanol, and 330 ns with isopropanol.
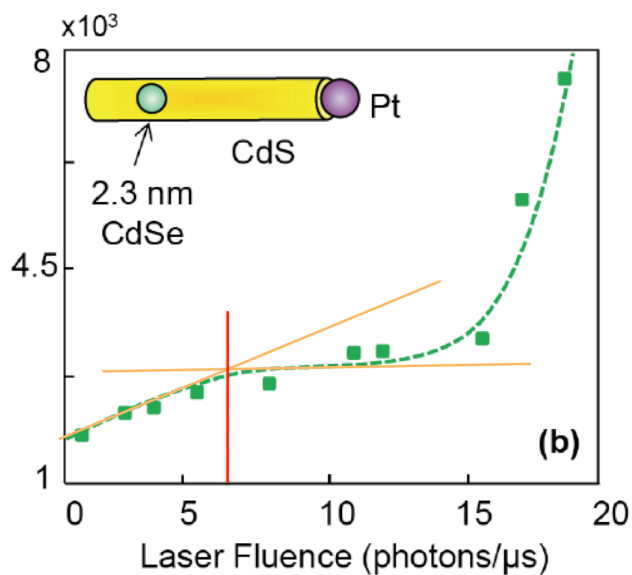
Fig. S7. Estimation of the saturation onset

Supporting Information References

SR1.   Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003,** *15,* 2854.

SR2.   Nirmal M., Dabbousi B.O., Bawendi M.G., Macklin J.J., Trautmaan, J.K. Harris T.D. and Brus L.E., Nature, **1996**, 383, 802.