

## Cadmium Selenide Quantum Wires and the Transition from 3D to 2D Confinement

Heng Yu,<sup>†</sup> Jingbo Li,<sup>‡</sup> Richard A. Loomis,<sup>†</sup> Patrick C. Gibbons,<sup>§</sup> Lin-Wang Wang,<sup>\*,‡</sup> and William E. Buhro<sup>\*,†</sup>

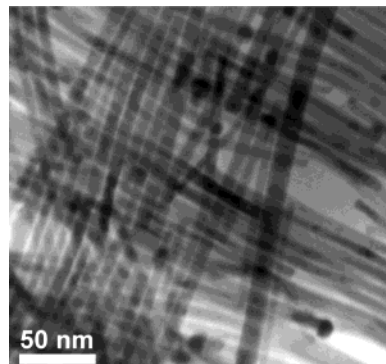
*Departments of Chemistry and Physics, Washington University, St. Louis, Missouri 63130-4899, and Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

Received August 16, 2003; E-mail: lwwang@lbl.gov; buhro@wuchem.wustl.edu

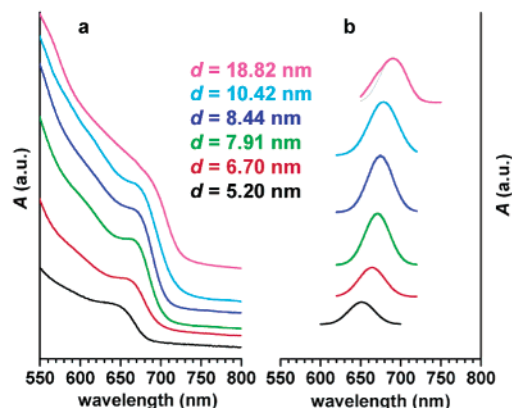
Here we report the size dependence of the band gaps in CdSe quantum wires and compare it to the corresponding size dependences in CdSe quantum dots and rods. We show that the experimentally measured quantum wire band gaps are consistent with theoretical predictions, confirming that geometric dimensionality influences quantum confinement as expected. Our results quantify true 2D quantum confinement in the well-studied CdSe system.

The recent availability of semiconductor nanocrystals having anisotropic rod,<sup>1–3</sup> wire,<sup>4,5</sup> arrow,<sup>6</sup> teardrop,<sup>6</sup> and tetrapod<sup>6,7</sup> morphologies has renewed interest in how shape affects the electronic and optical properties of quantum nanostructures.<sup>3,8,9</sup> Dots, rods, and wires provide compelling comparisons that explore the transition from simple 3D to 2D confinement.<sup>9</sup> This transition is revealed in the band gaps and their diameter dependences, both of which are larger in 3D-confined dots than in 2D-confined wires.<sup>5,9</sup> Electron–hole pairs in quantum rods are anisotropically 3D-confined, and therefore, rods constitute an intermediate case to dots and wires. Rods should exhibit 3D confinement in the short limit and 2D confinement in the long limit. Here we show that the confinement behavior of CdSe quantum rods is indeed delimited by that of CdSe dots and wires at the two length extrema. We also estimate experimentally the minimum length at which presently known<sup>2</sup> CdSe quantum rods have achieved the 2D confinement of a true quantum wire. That length ( $\sim 30$  nm) is surprisingly long in comparison to the bulk CdSe exciton Bohr radius ( $\sim 5$  nm).<sup>10</sup>

Solution–liquid–solid growth, as previously described,<sup>5,11,12</sup> afforded soluble (dispersible) CdSe quantum wires having fairly narrow diameter distributions and, to our knowledge, the smallest currently available diameters. The wires were prepared from cadmium stearate and *n*-R<sub>3</sub>PSe (R = butyl or octyl) in trioctyl phosphine oxide (TOPO) at 240–300 °C,<sup>13</sup> using monodisperse Bi nanoparticles<sup>14</sup> to catalyze wire growth. Control of wire diameters was achieved by varying the reaction temperature and the catalyst nanoparticle size. The wire dimensions were determined by transmission electron microscopy, which revealed micrometer lengths and diameters of  $d = 5$ –20 nm (Figure 1). Standard deviations in the diameter distributions ranged from 10 to 20% of the mean diameters, which were larger than the 5% standard deviations achieved in the best-quality quantum dots.<sup>15</sup> Electron diffraction patterns established that the wires were crystalline, with the 001 direction of the CdSe wurtzite crystal structure oriented along their long axis. The wires formed indefinitely stable red dispersions in TOPO and could be precipitated by methanol or 2-propanol addition and redispersed in toluene.



**Figure 1.** Representative transmission electron micrograph of CdSe quantum wires, mean diameter  $8.42 \pm 1.75$  ( $\pm 20.0\%$ ), grown at 255 °C.



**Figure 2.** (a) Representative absorption spectra of CdSe quantum wires; wire diameters ( $d$  values) are given in the key. (b) Lowest-energy excitonic peaks extracted by nonlinear least-squares fitting and background subtraction. The Gaussian fits to those peaks are the (scarcely evident) gray traces behind the peaks.

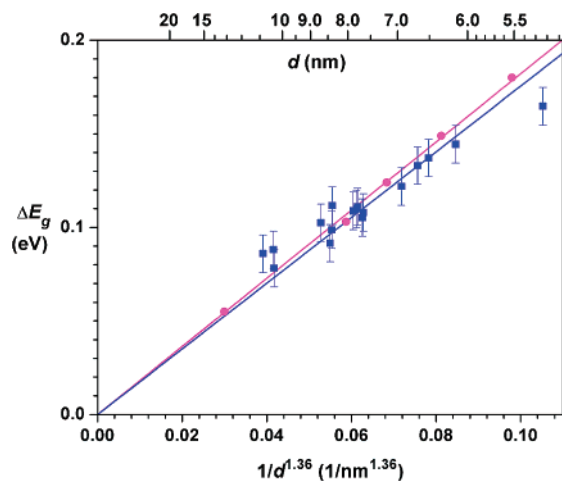
The quantum wire band gaps were determined from absorption spectra (Figure 2), recorded from toluene dilutions of the TOPO reaction mixtures. Excitonic features were clearly evident in the spectra. The lowest-energy feature in each spectrum was extracted by empirical nonlinear least-squares fitting. Band gap energies were assigned as the centers of the resulting Gaussian peaks and were plotted in Figure 3 as  $\Delta E_g$ , which is the increase in the band gap over the bulk value for CdSe (1.74 eV at 298 K).

For comparison to the experimental data, the CdSe quantum wire band gaps were also calculated by the plane-wave semiempirical pseudopotential method,<sup>5,16</sup> within the diameter range of  $d = 1.39$ –13.25 nm. Empirical fitting over the entire range established that the theoretical band gaps were proportional to  $1/d^{1.36}$ . Consequently, both the experimental and theoretical  $\Delta E_g$  values were plotted vs  $1/d^{1.36}$  in Figure 3, over the limited diameter range of

<sup>†</sup> Department of Chemistry, Washington University.

<sup>‡</sup> Lawrence Berkeley National Laboratory.

<sup>§</sup> Department of Physics, Washington University.



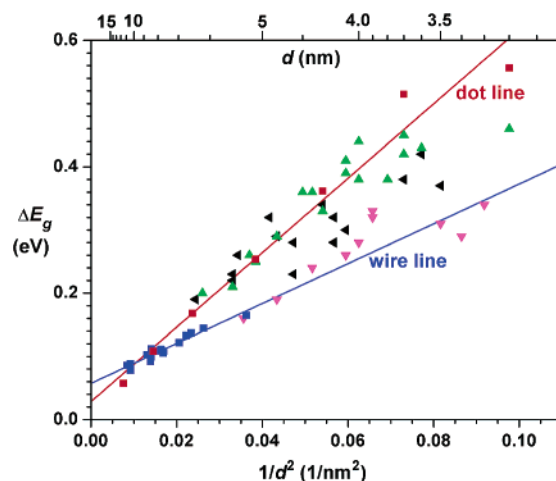
**Figure 3.** Experimental (blue squares) and theoretical (pink circles) band gap data for CdSe quantum wires plotted as  $\Delta E_g$  vs  $1/d^{1.36}$ . The blue and purple lines are linear least-squares fits, constrained through the origin, to the experimental and theoretical data, respectively.

mutual overlap in the two sets of band gap data. Linear least-squares fits (constrained through the origin) to the Figure 3 data gave the slopes  $A_{\text{theory}} = 1.82 \pm 0.01 \text{ eV nm}^{1.36}$  and  $A_{\text{exptl}} = 1.76 \pm 0.03 \text{ eV nm}^{1.36}$ . The excellent agreement between the experimental measurements and theoretical predictions established that the quantum wires exhibit band gaps consistent with the expectation for 2D confinement.

We now compare the size dependences of the band gaps in CdSe dots, rods, and wires. We previously argued<sup>5</sup> that, to a first approximation, the band gaps (and  $\Delta E_g$  values) of wells, wires, and dots should all scale linearly with  $1/d^2$ . This assertion was based on overly simple particle-in-a-box calculations of the kinetic confinement energies of electrons and holes. We further suggested<sup>5</sup> an approximate “rule of thumb” that in plots of  $\Delta E_g$  vs  $1/d^2$  for corresponding sets of dots and wires, the ratios of the slopes should be  $B_{\text{wire}}/B_{\text{dot}} = 0.585$ . As in the CdSe wire case above, the band gap energies of wires, dots, and rods *do not* scale precisely with  $1/d^2$  at higher levels of theory, but rather to other values of  $1/d^n$  (for example,  $n = 1.35$  and  $1.45$  for InP dots and wires, respectively).<sup>5</sup> However, because the true values of  $n$  vary with composition and the geometric dimensionality of confinement and are often unknown for lack of the semiempirical pseudopotential calculations required for each specific case, we believe the approximate scaling of  $\Delta E_g$  vs  $1/d^2$  and our rule of thumb provide a convenient common basis for comparing quantum confinement energies in corresponding sets of dots, rods, and wires.

Therefore,  $\Delta E_g$  values for CdSe quantum dots<sup>15</sup> and wires were plotted vs  $1/d^2$  in Figure 4. Linear least-squares fits to the two data sets gave the slopes  $B_{\text{wire}} = 3.15 \pm 0.20 \text{ eV nm}^2$  and  $B_{\text{dot}} = 5.89 \pm 0.43 \text{ eV nm}^2$  and the slope ratio  $B_{\text{wire}}/B_{\text{dot}} = 0.53 \pm 0.05$ . Note that this experimental  $B_{\text{wire}}/B_{\text{dot}}$  value is within experimental error of the rule-of-thumb prediction of 0.585 given above. We previously determined an analogous experimental slope ratio of  $0.62 \pm 0.03$  from the band gap data for InP wires and dots.<sup>5</sup> The CdSe and InP systems are the only two for which the diameter dependences of the band gaps of wires and dots have been systematically compared, and both comparisons were found to be consistent with our proposed rule of thumb.

The CdSe quantum rod  $\Delta E_g$  data<sup>2</sup> were also plotted vs  $1/d^2$  in Figure 4. As noted above, the quantum confinement in rods is intermediate to that in dots and wires; thus, the rod band gaps should be delimited by those of dots and wires of like diameter. Correspondingly, the  $\Delta E_g$  values for the rods fell within and close



**Figure 4.** Experimental CdSe quantum dot<sup>15</sup> (red squares) and quantum wire data (blue squares) plotted as  $\Delta E_g$  vs  $1/d^2$ . The red and blue lines are linear least-squares fits to the dot and wire data, respectively. The triangles correspond to CdSe quantum rods<sup>2</sup> of three length ( $l$ ) ranges:  $l = 7\text{--}15 \text{ nm}$ , green point-up triangles;  $l = 16\text{--}30 \text{ nm}$ , black point-left triangles;  $l = 31\text{--}44 \text{ nm}$ , pink point-down triangles.

to the Figure 4 region bound by the dot and wire lines. We surmised that the rod points clustered about the extrapolated quantum wire line (pink triangles, Figure 4) corresponded to rods of sufficient length ( $\geq 31.5 \text{ nm}$ ) to exhibit the 2D confinement of true quantum wires. Thus, the experimental data suggested that a length of approximately 30 nm was required for the third dimension of quantum confinement to fully vanish in CdSe rods<sup>2</sup> having diameters of 3–6 nm. Interestingly, that length is about 6 times the bulk CdSe exciton Bohr radius,<sup>10</sup> not just one or two multiples of it as suggested by theory (see Figure 1b in ref 8).

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**Supporting Information Available:** Experimental and theoretical methods, diameter distribution histograms, diffraction patterns, and tables of spectroscopic and theoretical data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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