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LETTERS

Assemblies of CdS Quantum Particles Studied by the Attenuated Low Energy Photoelectron Spectroscopy

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We report on the direct observation of collective electronic properties in assembled CdS quantum particles (QPs) arranged in periodic layers. Within each layer the QPs are of the same average size, either 2.5 or 5 nm, and the layers are arranged in a cascade-like pattern. The electronic properties of the QPs were studied using a new method, the attenuated low energy photoelectron spectroscopy (A-LEPS), in which a “pump” laser excites the QPs and a “probe” laser ejects photoelectrons from the QPs and from the metal substrate. The A-LEPS method provides information about the populated electronic states of the QPs (including the splitting between the light/heavy hole and split-off bands) and how these states depend on the interparticle interactions.

Semiconductor quantum particles (QPs) that range in size typically from 1 to 10 nm are continuing to attract interest due to their unique electronic,^{1–4} optical,^{5–7} and catalytic^{8,9} properties. The ability to control the size and organization of QPs in the form of superlattices has also received attention recently.¹⁰ Any attempt to utilize QPs arranged within superlattices must consider the effects of the surroundings on the electronic properties of the QPs. Indeed, numerous studies on this subject have been performed using various methods such as photoluminescence,^{11,12} transient absorption,^{13,14} transient excitonic bleaching,¹⁵ valence-band photoemission,¹⁶ and X-ray photoemission from the core levels of the QPs.^{10,17}

Here we report on a *direct* observation of the effects induced by the *surroundings* on the electronic properties of assembled CdS QPs. Our approach combines new preparation and characterization techniques; the preparation procedure is highly controllable, and the spectroscopic method provides information on a wide spectral range and therefore is complementary to the existing techniques. The results provide clear evidence for the

interaction between the QPs in the matrix and between them and the substrate.

The assembled QPs were prepared in matrixes containing six layers of hybrid CdS QPs embedded within Langmuir–Blodgett (LB) films of variable mixtures of arachidic or thioarachidic acids (the details are reported elsewhere¹⁸). The LB films were deposited on gold substrate and were inserted into an ultrahigh vacuum chamber that can be pumped to a pressure lower than 10^{–8} mbar. Three types of structures were prepared (see Scheme 1), either a matrix containing single size particles of average diameters 2.5 (Scheme 1d) or 5 nm (Scheme 1a), or matrixes containing three layers of one size and three layers of the other size of QPs (Scheme 1, parts b and c).

The electronic properties of the assembled QPs were studied using a new technique, the attenuated low energy photoelectron spectroscopy (A-LEPS), in which the LEPS signal^{19–21} is attenuated by electronic excitation of the QPs. Thus, in the A-LEPS method we applied a “pump” laser which operated in the visible or near-UV (Quanta-Ray Pro 230, Nd: Yag pumped dye laser with frequency doubling and tripling) to excite the QPs, in addition to the “probe” UV laser (Lambda Physik excimer laser, Compex 102, operated at 193 nm) which ejected photoelectrons from both the metal substrate and from the QPs.

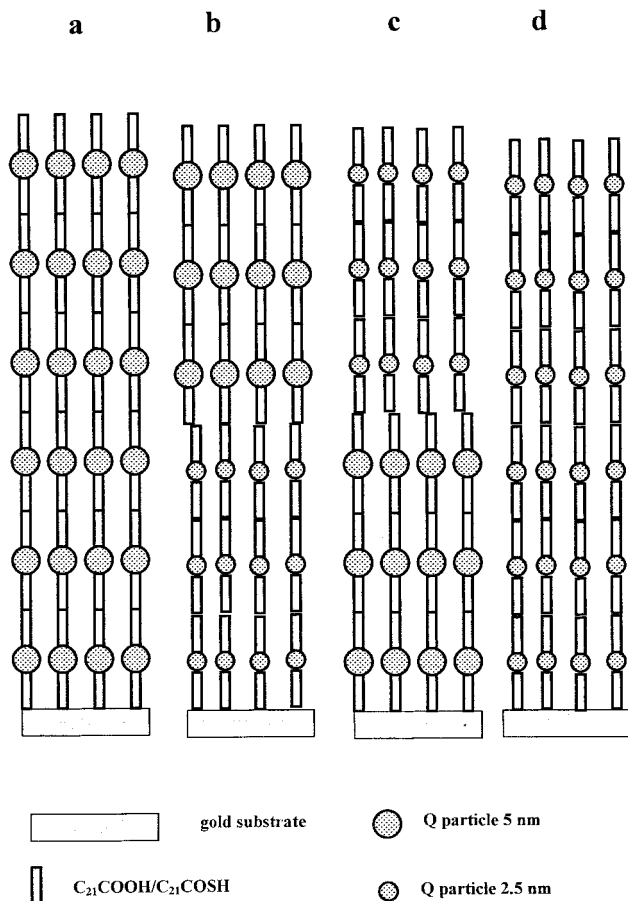
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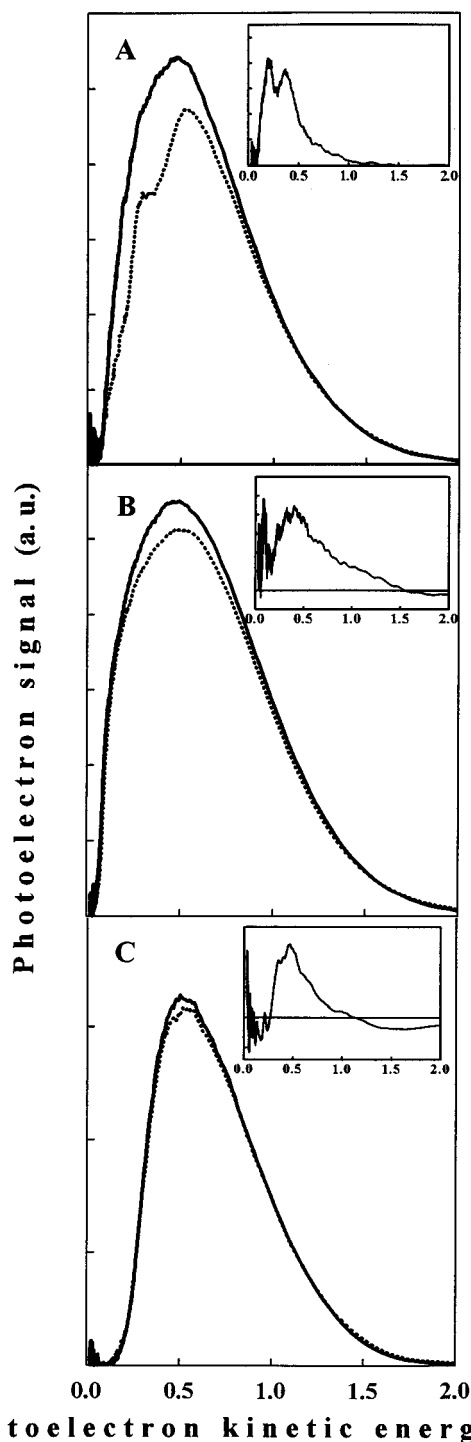
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SCHEME 1: Schematic Representation of the Cascade-like Hybrid Organic CdS films. The Lines Represent the Organic Molecules, either Arachidic or Thioarachidic Acid. (A) A Scheme of 6 Layers of Large (diameter of 5 nm) QPs. (B) Three Layers of Large on Top of 3 Layers of Small (diameter of 2.5 nm) QPs. (C) Three Layers of Small on Top of 3 Layers of Large QPs. (D) 6 Layers of Small QPs



We then analyzed the energy distribution of the emitted electrons with and without the “pump” laser using a time-of-flight spectrometer, with resolution of about 30 meV. To avoid any charging of the film or multiphoton effects we used very low lasers power (300 and 30 nJ for the pump and probe lasers respectively). The “pump laser” wavelength was chosen to be 532 and 355 nm since at 532 nm only the large QPs absorb, while at 355 nm both particles have absorption.¹⁸

In Figure 1 A,B we show the photoelectron spectra for film 1a containing six layers of large particles. The pump laser was set to 532 nm (A) or 355 nm (B), and the probe laser was set to 193 nm in both cases. The difference between the spectra obtained with and without the “pump” laser is shown in the inset for each case. Depletion in the spectrum was observed when the film containing the QPs was illuminated at 532 nm. Upon excitation at 355 nm, in addition to the depletion we observed a small enhancement in the signal for electrons with energy above 1.5 eV. Note that our samples are not uniform in size and shape, and the 355 nm light excites a wider range of particle size. As will be discussed below, the excited-state lifetime of the small particles is longer than that of the large particles. Therefore, we attribute the enhancement observed in the A-LEPS for the 355 nm excitation as due to the excitation of relatively small particles having a long excited-state lifetime.



Photoelectron kinetic energy, eV

Figure 1. The photoelectron spectra obtained for a film 1a (6 layers of 5 nm particles) when illuminated with a light at 532 nm (A) or 355 nm (B) and when film 1d (6 layers of 2.5 nm particles) is illuminated at 355 nm (C) in addition to the 193 nm photon. The solid lines are the LEPS obtained without the pump laser, while the dotted lines are spectra obtained with the two lasers on. In the insets the difference spectra are shown when the signal obtained with the two lasers (193 and 355 nm or 532 nm) is subtracted from that obtained with the 193 nm laser alone.

Both the depletion and enhancement occurred only if the two lasers overlap in time. No effect of the “pump” laser was observed if the delay between laser pulses exceeds their pulse length, implying that the lifetime of the excited species is shorter than several nanoseconds and in agreement with previous experimental studies.^{12,13} The line width observed may relate to a short lifetime, supported by broader lines obtained when

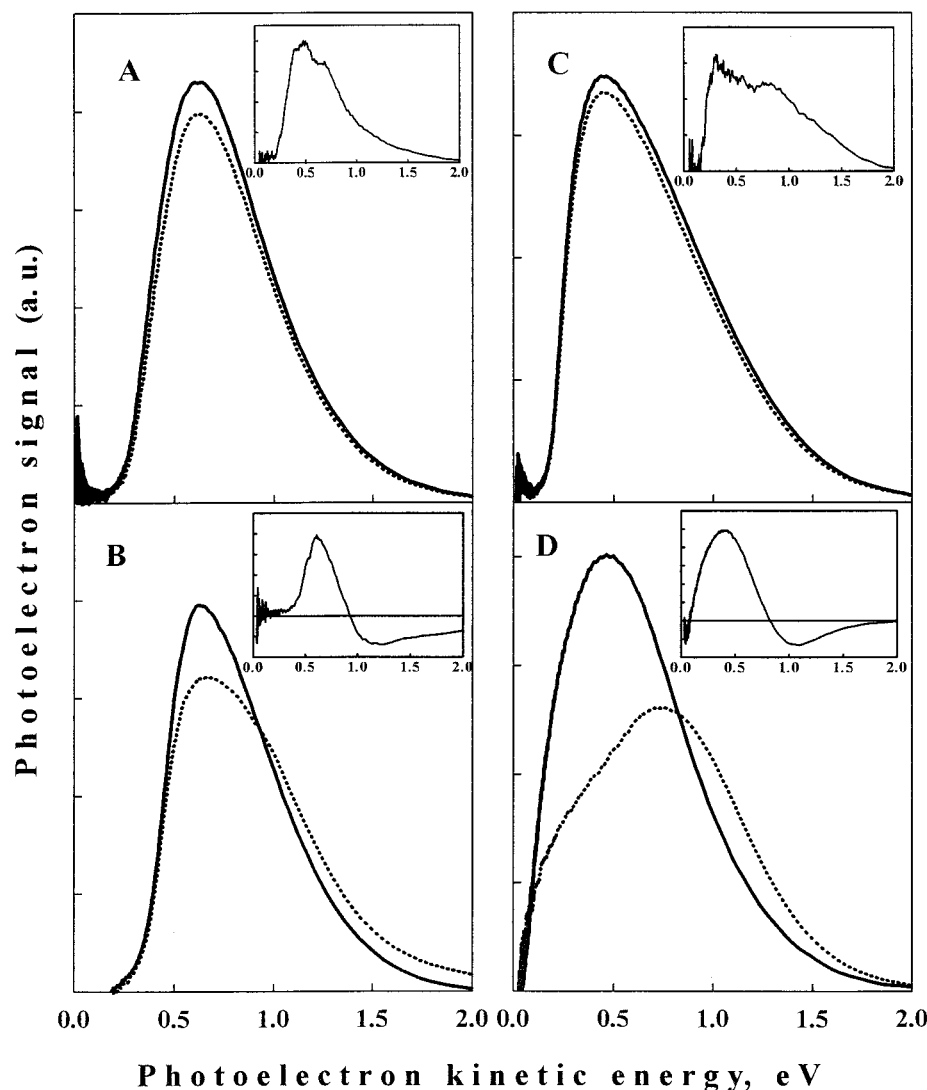


Figure 2. The photoelectron spectra obtained with films 1b (3 layers of 5 nm particles on top of 3 layers of 2.5 nm particles) or 1c (3 layers of 2.5 nm particles on top of 3 layers of 5 nm particles) when the sample was illuminated both at 532 and 193 nm (dotted line), A and C, respectively. For comparison, the spectra obtained with the 193 nm alone are also shown (solid line). Figure 2, parts B and D, were obtained when the samples 1b and 1c, respectively, were illuminated with 355 and 193 nm. In the inset in each figure we show the result of subtracting the signal obtained when both pump and probe lasers are applied from that obtained with a single 193 nm laser.

excitation occurs at 355 nm (inset Figure 1B). However, the asymmetry in the width indicates that at least partially it results from inhomogeneous broadening due to the presence of other states, presumably surface states.

The probe laser ejects electrons from both the QPs and from the metal substrate; however, the difference spectrum provides information *only* on the populated states of the QPs (indeed the difference spectrum vanished when the film did not contain any QPs). Since the ionization laser has energy of about 6.42 eV and the photoelectron spectrum is depleted at kinetic energies of 0.4 and 0.2 eV, the two peaks in the spectrum (Figure 1A) correspond to states lying at about 6.0 and 6.2 eV below the ionization potential of the QPs. The value of the energy of these states is strong evidence that these are intrinsic states of the QPs and not surface states with energy well inside the band gap. However, absorption experiments at 532 nm indicate the existence of surface states (or intrinsic gap states²²), namely, there is a transition in the QPs that corresponds to energy of about 2.3 eV below the bulk excitonic gap (2.59 eV). This states were also observed in the absorption spectrum shown in ref 18. The organic molecules in the film were not ionized, since

the maximum photon energy used was set to 6.42 eV, far below their ionization potential.

The photoelectron spectrum for film 1d when illuminated at 355 nm is shown in Figure 1C. Upon illumination with the two lasers, we observed reduction in the signal for electrons with kinetic energy below 1.1 eV and moderate enhancement for electrons with higher energies. The enhancement peaks at electron energy of about 1.5 eV, approximately 1 eV above the states that are depleted. This means that there is a relatively long-lived excited state that is located at about 1 eV above the ground state, in agreement with previous photoluminescence studies, where emission at the same wavelengths^{18,23} was attributed to the recombination of trapped charge carriers. In general we see that for the large particles excitation causes mainly depletion in the intensity of the signal. However, in the case of small particles, excitation causes depletion of low-energy electrons and enhancement of electrons at high energies. This means that the lifetime of the excited state of the small particles is long enough to allow sequential excitation and photoelectron ejection from the excited state. In contrast, for large QPs the

lifetime of the excited states is short due to the strong interaction with the substrate and the matrix.

Our current assignment of the observed doublet states (Figure 1, panel A) is based on the tight-binding model.²⁴ The tight-binding model, which includes spin-orbit (SO) interaction, leads to a splitting of the topmost valence band into two states. The separation between the top valence states is mainly attributed to the spin-orbit coupling. In the so-called two band effective mass approach²⁵ the splitting is between the light/heavy hole ($1S_{3/2}(h)$) and the split-off ($1S_{1/2}(h)$) bands. Our observed energy separation between these two states is somewhat larger (0.2 eV) than the theoretical prediction of the tight-binding model (0.05 eV) for similar size nanoparticles. There are several possible reasons for this difference. First, the shape of the QPs is not perfectly spherical. In fact TEM images of the particles show that they are elongated in the direction of the film.¹⁸ Second, the interactions between QPs within a given layer due to the lack of passivation may also contribute to the difference between the experiments and theory. Finally, the presence of the metal substrate can change the valence electronic density of states.²⁶ We note that the spin-orbit splitting obtained from an empirical pseudopotential method²⁷ shows a significant dependence of the splitting with particle size, and the value of the spin-orbit splitting calculated agrees well with our experimental observation.

In Figure 2 we show the photoelectron spectra obtained for films 1b and 1c. Panels A and C were obtained when the samples were illuminated at both 532 and 193 nm, and panels B and D were obtained when illuminating with 355 and 193 nm lasers. The inset of each figure shows the result of subtracting the signal taken with the two lasers from that taken with a single 193 nm laser (difference spectrum). The results depicted in each pair (2A,C and 2B,D) are different despite the fact that the two samples have the same composition, and the only difference is the sense of polarity of the cascade-like pattern vis-a-vis the substrate.

When the 532 nm laser was applied, only the large particles in each film were excited. The photoelectron signal was reduced when the two lasers were turned on compared to the single laser experiment. Furthermore, in both Figure 2A and 2C the difference spectra are wider as compared to the difference spectrum in the inset of Figure 1A. The broadest spectrum was obtained when the large particles were near the substrate (Scheme 1c, Figure 2C), indicating the strong interaction between the large particles and the substrate. When the 355 nm laser was applied, both large and small QPs were excited and the signal was reduced for electrons with energy up to about 0.8 eV, but was enhanced for higher energies. Similar to the previous case we observe differences between the two films. While the cutoff in the difference spectrum starts at about 0.3 eV for the 1b (inset Figure 2B), in the case of the 1c film it starts from the origin (inset Figure 2D). The results in Figure 2B are similar to those in Figure 1C where a film containing only small particles was studied. *This is an indication that the cutoff is affected mainly by the particles that are near the substrate.* This generates a clear asymmetry in the spectra of the two structures shown in Schemes 1b,c, and the electronic structure of the film containing QPs of both sizes depends on which of the QPs is on the bottom, namely close to the substrate.

When a spacer of organic molecules was placed between the lower QPs layers and the substrate, the asymmetry vanished.

In conclusion, the A-LEPS method provides direct measure for the populated electronic states of the QPs, and in addition it provides a clear signature for the interactions between CdS QPs in the film. The collective electronic properties of the assembled QPs are clearly seen if one compares Figure 1 to Figure 2. The A-LEPS signal for the films containing small and large QPs is *not* simply a superposition of the signal observed for the large and the small particles alone. This means that the excited state of the particles is clearly affected by the existence of other particles in the matrix as well as by the nearby substrate.

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References and Notes

- (1) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
- (2) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183.
- (3) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525.
- (4) Weller, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 41.
- (5) Wang, Y. *Acc. Chem. Res.* **1991**, *24*, 133.
- (6) Rosencher, E.; Fiore, A.; Vinter, B.; Berger, V.; Bois, P.; Nagle, J. *Science* **1996**, *271*, 168.
- (7) Hines, M. A.; Guyot-Sionnest, P. *J. Phys. Chem. B* **1996**, *100*, 468.
- (8) Bard, A. J. *Science* **1980**, *207*, 4427.
- (9) Yanagida, S.; Yooshyia, M.; Shiragami, T.; Pac, C. J.; Mori, H.; Fujita, H. *J. Phys. Chem.* **1990**, *94*, 3104.
- (10) Heitmann, D.; Kotthaus, J. P. *Phys. Today* **1993**, *46*, 56. (b) Fendler, J. H. *Nanoparticles and nanostructured films: preparation, characterization and applications*; Wiley-VCH: Weinheim, 1998. (c) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221. (d) Motte, L.; Billoudet, F.; Lacaze, E.; Douin, J.; Pileni, M. P. *J. Phys. Chem. B* **1997**, *101*, 138. (e) Guo, S.; Popowitz-Biro, R.; Arad, T.; Hodes, G.; Leiserowitz, L.; Lahav, M. *Adv. Mater.* **1998**, *10*, 657.
- (11) Kuno, M.; Lee, J. K.; Dabbousi, B. O.; Mikulec, F. V.; Bawendi, M. G. *J. Chem. Phys.* **1997**, *106*, 9869.
- (12) Micic, O. I.; Cheong, H. M.; Fu, H.; Zunger, A.; Sprague, J. R.; Mascarenhas, A.; Nozik, A. J. *J. Phys. Chem. B* **1997**, *101*, 4904.
- (13) Roberti, T. W.; Cherepy, N. J.; Zhang, J. Z. *J. Chem. Phys.* **1998**, *108*, 2143.
- (14) Klimov, V. I.; Schwarz, Ch. J.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. *Phys. Rev. B* **1999**, *60*, 2177.
- (15) See for example, Wang, Y.; Suna, A.; McHugh, J.; Hilinski, E. F.; Lucas, P. A.; Johnson, R. D. *J. Chem. Phys.* **1990**, *92*, 6927.
- (16) Colvin, V. L.; Alivisatos, A. P.; Tobin, J. G. *Phys. Rev. Lett.* **1991**, *66*, 2786.
- (17) Nanda, J.; Kuruvilla, B. A.; Sarma, D. D. *Phys. Rev. B* **1999**, *59*, 7473.
- (18) Guo, S.; Konopny, L.; Popowitz-Biro, R.; Cohen, H.; Porteanu, H.; Lifshitz, E.; Lahav, M. *J. Am. Chem. Soc.* **1999**, *121*, 9589.
- (19) Kadyshkevitch, A.; Naaman, R. *Phys. Rev. Lett.* **1995**, *74*, 3443.
- (20) Kadyshkevitch, A.; Naaman, R. *Thin Solid Films* **1996**, *288*, 139.
- (21) Naaman, R.; Haran, A.; Nitzan, A.; Evans, D.; Galperin, M. *J. Phys. Chem. B* **1998**, *102*, 3658.
- (22) Sercel, P. C.; Efros, Al. L.; Rosen, M. *Phys. Rev. Lett.* **1999**, *83*, 2394.
- (23) Ramsden, J. J.; Webber, S. E.; Grätzel, M. *J. Phys. Chem.* **1985**, *89*, 2740. Chamarro, M.; Dib, M.; Voliotis, V.; Filoramo, A.; Roussignol, P.; Gacoin, T.; Boilot, J. P.; Delerue, C.; Allan, G.; Lannoo, M. *Phys. Rev. B* **1998**, *57*, 3729.
- (24) Ramaniah, L. M.; Nair, S. V. *Phys. Rev. B* **1993**, *47*, 7132.
- (25) Ekimov, A. I.; Onushchenko, A. A.; Plyukhin, A. G.; Efros, Al. L. *SoV. Phys. JEPT* **1985**, *61*, 891.
- (26) Krauss, T. D.; Brus, L. E. *Phys. Rev. Lett.* **1999**, *83*, 4840.
- (27) Tomasulo, A.; Ramakrishna, M. V. *Chem. Phys.* **1996**, *210*, 55.