Size-quantized Semiconductor Particles formed at Monolayer Surfaces

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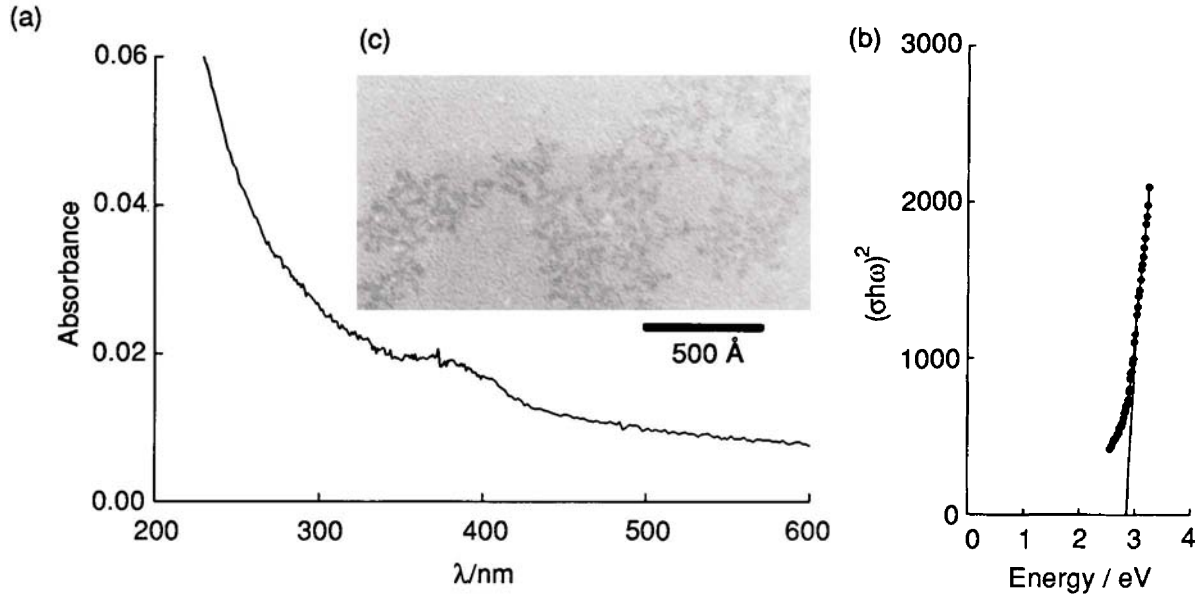
Infusion of H_2S onto cadmium arachidate, zinc arachidate, or metal-ion-coated poly(styrenephosphonate diethyl ester) monolayers resulted in the formation of size-quantized semiconductor particles which could be transferred, essentially intact, to solid substrates at different stages of their growth; scanning tunnelling microscopy, transmission electron microscopy, and absorption spectrophotometry established the initial formation of 25–30 Å diameter particles which aligned themselves and grew laterally to linked, 50–100 Å diameter, 20–30 Å thick, disk-shaped polyparticles.

We report here that the controlled infusion of H_2S onto appropriate metal counterion-coated monolayers results in the formation of size-quantized semiconductor particles[1,2] which can be transferred to solid substrates at different stages of their growth. Arachidic acid, $Me(CH_2)_{18}CO_2H$ (Sigma), was purified by recrystallization from ethanol. Preparation of poly(styrenephosphonate diethyl ester) (PSP), has been described.[3] $CdCl_2$ and $ZnCl_2$ (Baker Analyzed Reagents), H_2S (Matheson Gas Products), and $CHCl_3$ (Aldrich) were used as received; water was purified by a Millipore Milli-Q system provided with a 0.22 μm Millistack filter at the outlet.

Monolayers were compressed to 20 Å^2/molecule in a



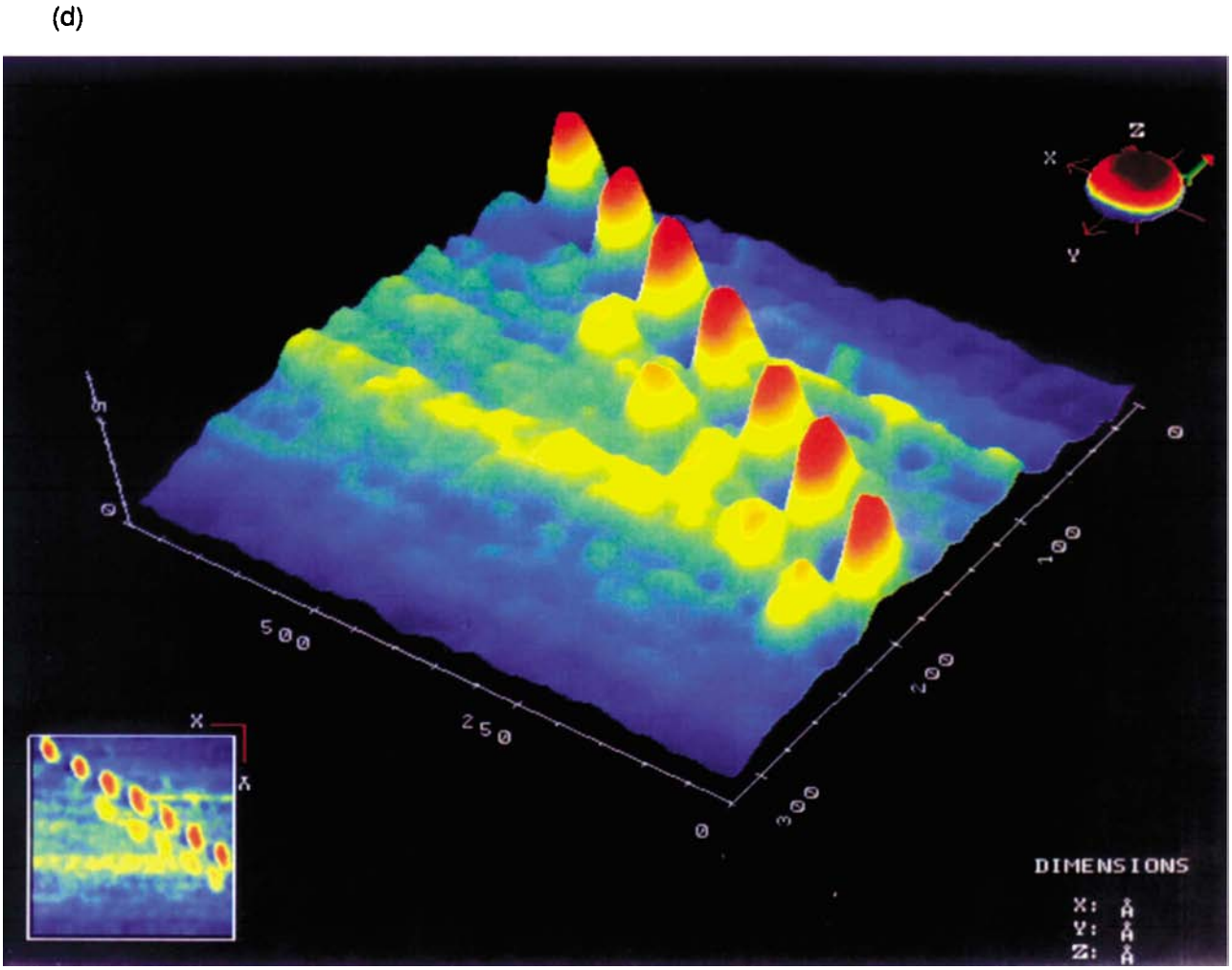


Fig. 1 (a) Absorption spectrum of CdS particles, generated *in situ* at PSP monolayer interfaces. The subphase contained 1.0×10^{-3} M $CdCl_2$ and the monolayer was kept at 20 $Å^2$/molecule pressure. Transfer to quartz was effected after 3 min of exposure to H_2S. (b) A plot of $(\sigma h\omega)^2$ against energy. (c) Transmission electron micrograph of CdS particles, formed *in situ* under identical conditions and subsequently transferred to a celluloid-coated copper grid (200 mesh). (d) Three-dimensional STM images of CdS particles on HOPG, formed *in situ* on cadmium arachidate monolayers (kept at 20 Å/molecule pressure) by three minutes of exposure to H_2S. Insert, a bird's eye view of the same area in two dimensions (x and y axes are on the same scale as in the three-dimensional plot)

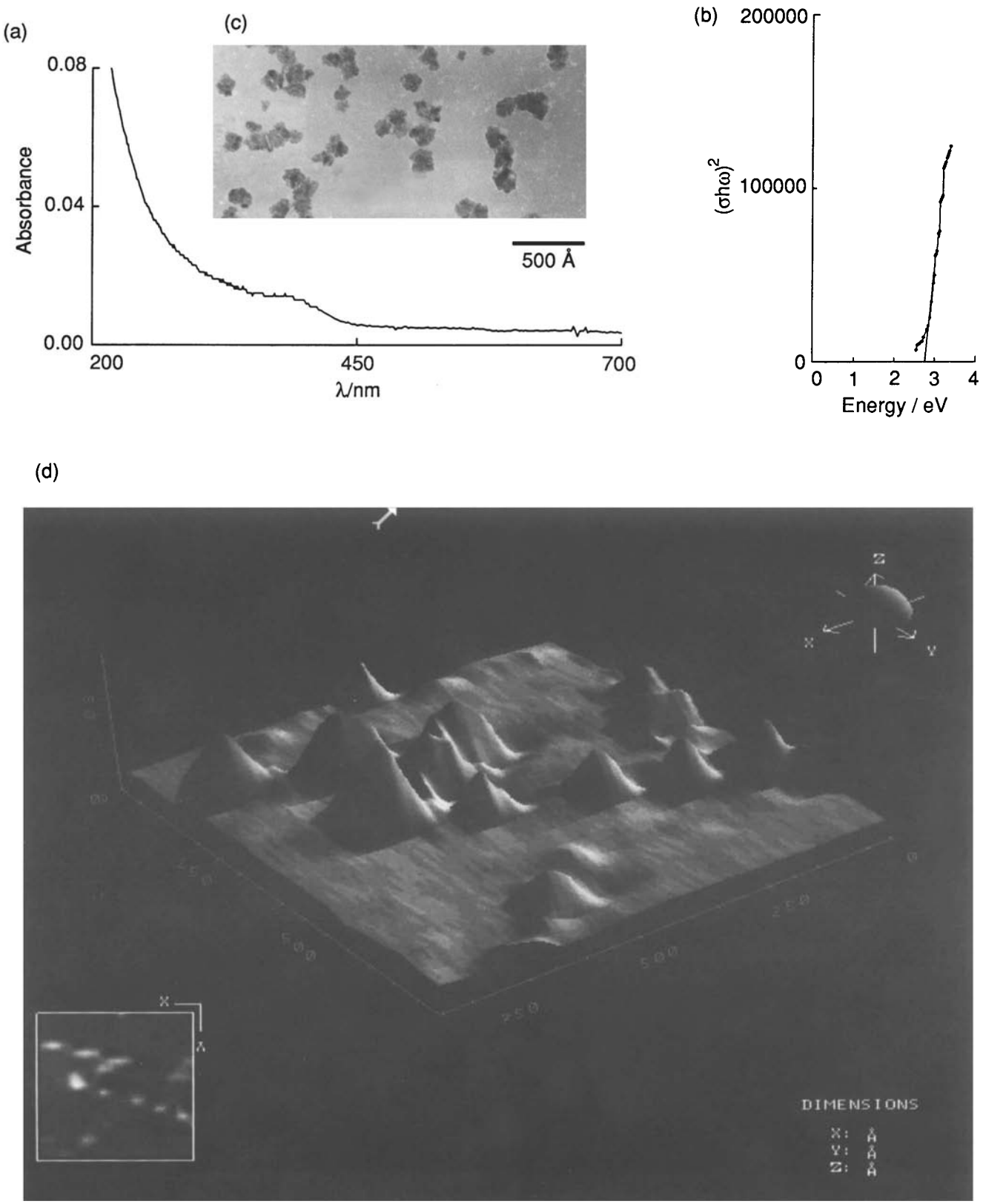


Fig. 2 As for Fig. 1, except transfer to quartz occurred after 15 min of exposure to H_2S

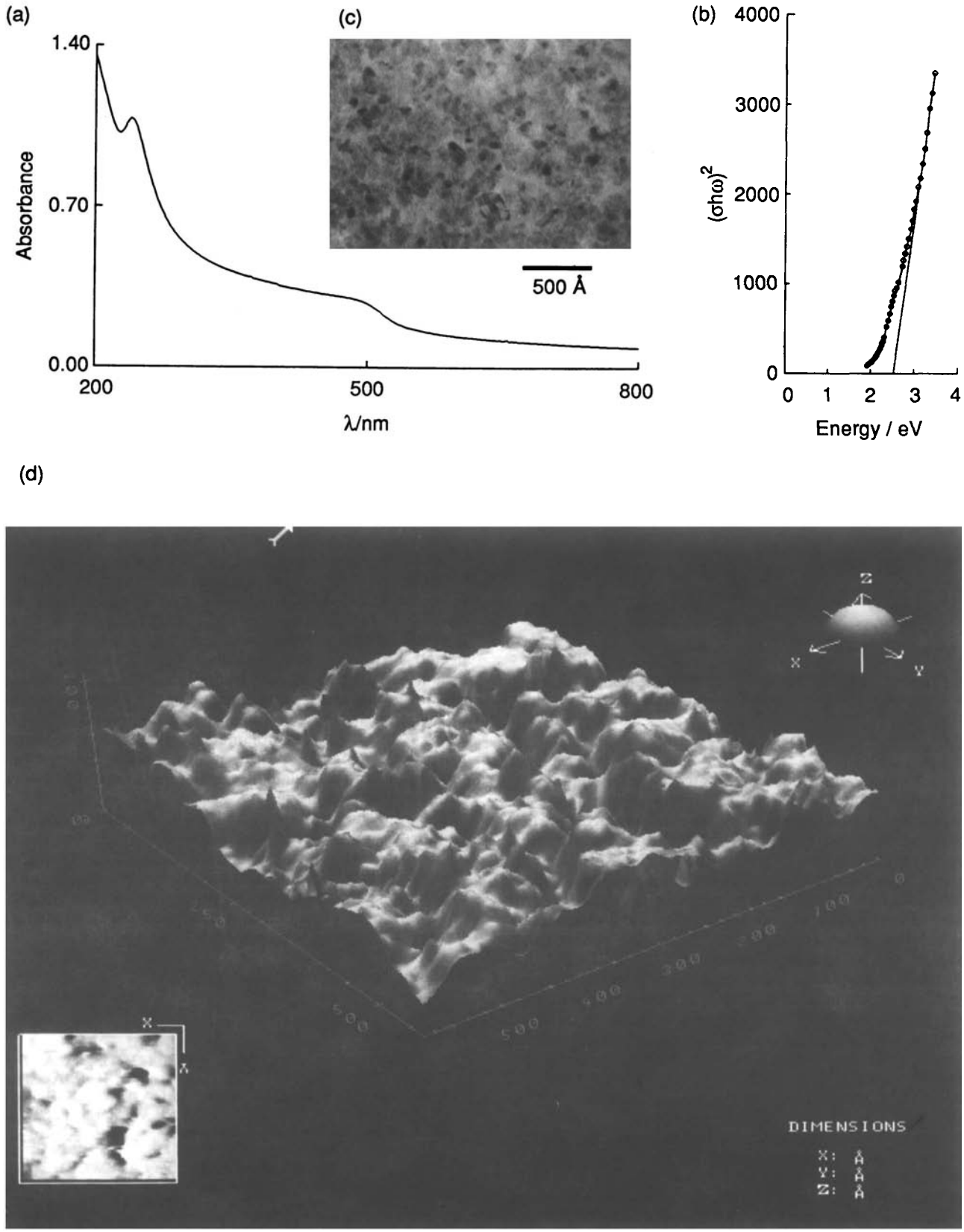


Fig. 3 As for Fig. 1, except transfer to quartz occurred after 30 min of exposure to H_2S

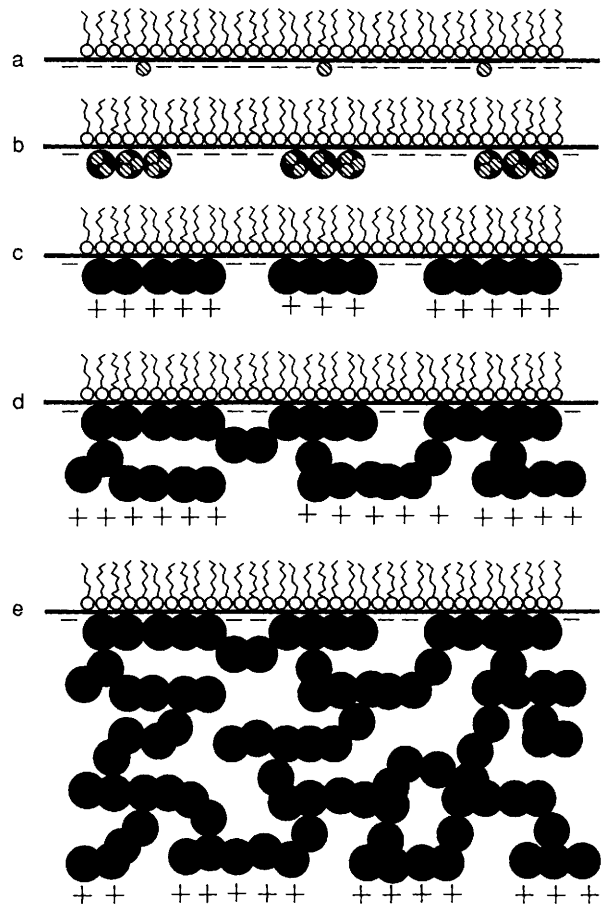


Fig. 4 Proposed scheme for the initial (a) and subsequent (b–e) growth of a monolayer-supported, porous, semiconductor particulate film

circular trough. Introduction of hydrogen sulphide onto compressed monolayers resulted in the formation of the semiconductor particles at the monolayer interface;[4] particle formation was monitored by reflectivity measurements.[5] Twenty to thirty minutes after the introduction of H_2S, a faint fog-like layer became observable at the monolayer interface. Continuous slow infusion of H_2S increased the intensity of the reflected light until a plateau value (at *ca.* 10 h of infusion), was reached which corresponded to limiting optical thicknesses of 250–300 and 1600–1800 Å for CdS and ZnS.

Monolayer-supported particulate films were transferred, essentially intact, to solid substrates at different times during their growth by horizontal lifting. Well cleaned quartz (chromic acid, dust-free water), highly oriented pyrolytic graphite (HOPG, Union Carbide, freshly cleaved), and celluloid-coated copper grids were used as substrates for absorption spectrophotometry, scanning tunnelling microscopy, and transmission electron microscopy, respectively. Scanning tunnelling microscopic images were acquired by means of an Angstrom Technology (Mesa, Arizona) TAK 3.0 instrument operated in the constant current mode; a platinum wire was used for the tunnelling tip. Images were scanned with five lines per second ±0.5 volts tip bias and were plotted on a CP 200U Mitsubishi colour videocopy processor. After the films had been transferred to graphite, they were dried for 24 h and surfactant monolayers were removed by gentle rinsing with $CHCl_3$, ethanol, and dust-free water. Eight separately prepared samples of CdS and ZnS were investigated. Images were taken for each sample in 10–100 different areas. A Hewlett-Packard 8450A diode array spectrophotometer was used to record the absorption spectra. Transmission electron micrographs were taken on a JEOL JEM-2000 EX 120 keV instrument.

The absorption spectrum, plot of the data according to $(\sigma h\omega)^2 = h\omega C - E_g C$ (where σ is the absorption coefficient, $A = \sigma d$ where A is the absorbance and d is the optical thickness of the semiconductor particulate film determined from reflectivity measurements, and $h\omega$ is the photon energy), and transmission electron micrograph of CdS particles, generated *in situ* at cadmium ion-coated PSP interfaces, after three minutes of H_2S exposure are shown in Fig. 1. The observed absorpion threshold (λ_t), 445 nm, or direct band-gap (E_g), 2.83 eV, led to an assessment of 30 Å for the mean diameter of the CdS particles from Henglein's published λ_t or E_g *vs.* particle size curve.[6] As seen in the insert, transmission electron micrographs nicely support the presence of 30 ± 5 Å particles.

STM has been most informative as it allowed the three-dimensional visualization of the nascent semiconductor particles in their earliest stages of aggregation. Early stages of growth of CdS particles, generated *in situ* on cadmium arachidate surfaces, are illustrated in Fig. 1. Images were taken after 3 (Fig. 1), 15 (Fig. 2), and 30 (Fig. 3) min. of H_2S infusion onto the compressed cadmium arachidate monolayer. Conical, well separated CdS microclusters of 30–60 Å diameter and 5–8 Å height are seen to align themselves laterally in Fig. 1. Longer infusion of H_2S allowed the lateral growth of the microclusters and their coalescence to interconnected arrays of particles whose mean diameters were established to be 55–80 Å by transmission electron microscopy and absorption spectrophotometry (Fig. 2). Continued growth in thickness led to a contiguous film composed of porous, 20–30 Å thick, 75–100 Å diameter, disk-shaped semiconductor particles (Fig. 3). A proposed model for the growth of semiconductor particulate film, generated *in situ* at monolayer surfaces, is shown in Fig. 4.

The convenient preparation of fully characterizable, size-quantized semiconductor particles reported here could lead to solid-state devices with beneficial optical, electro-optical, electrical, and photoelectrical behaviour. We are continuing exploration of the fundamental properties of these systems.

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