Control of Size and Composition of Chalcogenide Colloids in Langmuir–Blodgett Films

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The generation of Q-state particles of CdS, CdSe, CdTe and CdS_xSe_{1-x} in polymerized nonacosa-10,12-diynoic acid, Langmuir–Blodgett (LB) films is described; particle size can be varied by mixing the diynoic acid with dihexadecyl phosphate and preparing the cast films from a subphase containing a mixture of $CdCl_2$ and $CaCl_2$.

The preparation of semiconductor particles with diameters less than about 50 Å (Q-state particles) usually produces particles displaying size quantization effects, manifested by shifts (relative to the bulk material) in the optical bandgap,[1] redox levels of the conduction and valence bands,[2] and the material's linear and non-linear optical properties.[3]

Although it is general practice to generate Q-state particles in solution, they may also be produced in Langmuir–Blodgett (LB) films.[4] The advantage of the latter mode of preparation is that the particles are in a matrix that lends itself to coating optical fibres or plates. Mechanical and chemical robustness of the films and control of the size and chemical composition of the particles are elements that can enhance the overall utility of Q-state particle films. With this in mind we have prepared polymerized LB films using nonacosa-10,12-diynoic acid (16–8 diynoic acid) doped with quantized CdS, CdSe, CdTe and CdS_xSe_{1-x} colloids.

LB films of cadmium 16–8 diynoate were prepared using a conventional 'Teflon' Langmuir trough and a Lauda film-lift system.[5] Monolayer casting onto hydrophobed (using trimethylchlorosilane) silica plates was carried out at a constant air-water film pressure of 20 mN m^{-1} at pH = 6.9 (buffered with sodium hydrogencarbonate), on a $CdCl_2$ (10^{-3} mol dm^{-3}) subphase. Coated plates were exposed to H_2X (X = S, Se or Te) for several minutes in a sealed, nitrogen purged, container. Fig. 1 shows the absorption spectra of the 16–8 diynoic acid films after exposure to the stated gases. The insert shows the absorption spectra after exposing the LB film (under N_2) to UV radiation (2–4 min, at 1 mW cm^{-1}, rated at 254 nm) and subsequent heating (10 min at 100 °C). The spectra are characteristic of the blue and red forms of the 16–8

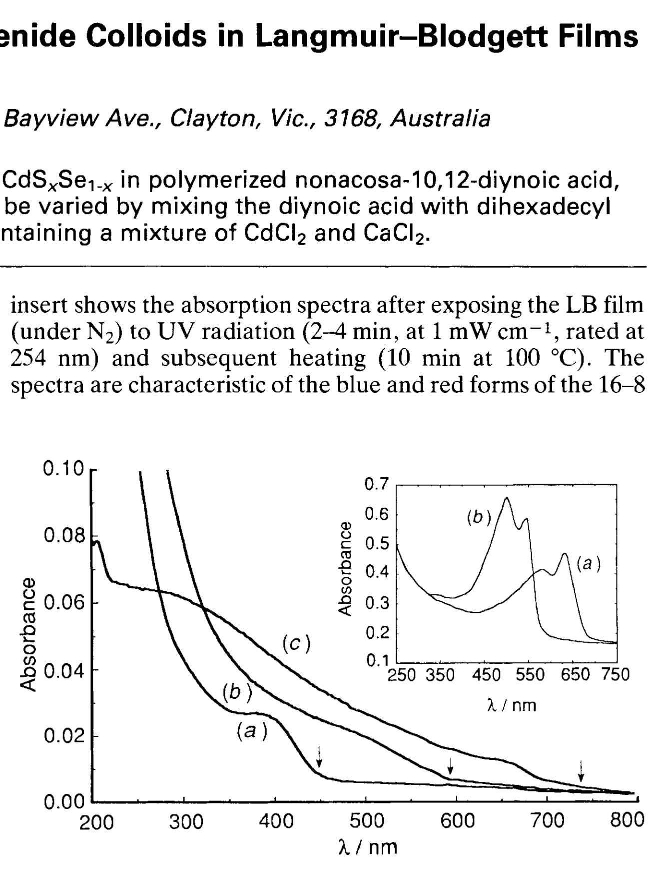

Fig. 1 Absorption spectra of 19 layer 16–8 diynoic acid films, deposited from a subphase of $CdCl_2$ (10^{-3} mol dm^{-3}; pH 6.9) at a surface pressure of 20 mN m^{-1}, after exposure to (*a*) H_2S; (*b*) H_2Se and (*c*) H_2Te. The shoulder around 650 nm on curve (*c*) is due to some 16–8 diynoic acid polymer. All curves have been corrected for background absorption. The arrows indicate the position of the bandgaps of the respective semiconductor particles. Insert: absorption spectra of a 7 layer 16–8 diynoic acid film, deposited from a subphase of $CdCl_2$ (10^{-3} mol dm^{-3}; pH 6.9), exposed to H_2S and (*a*) UV irradiated for 2 min; (*b*) *a* heated at 100 °C for 5 min.

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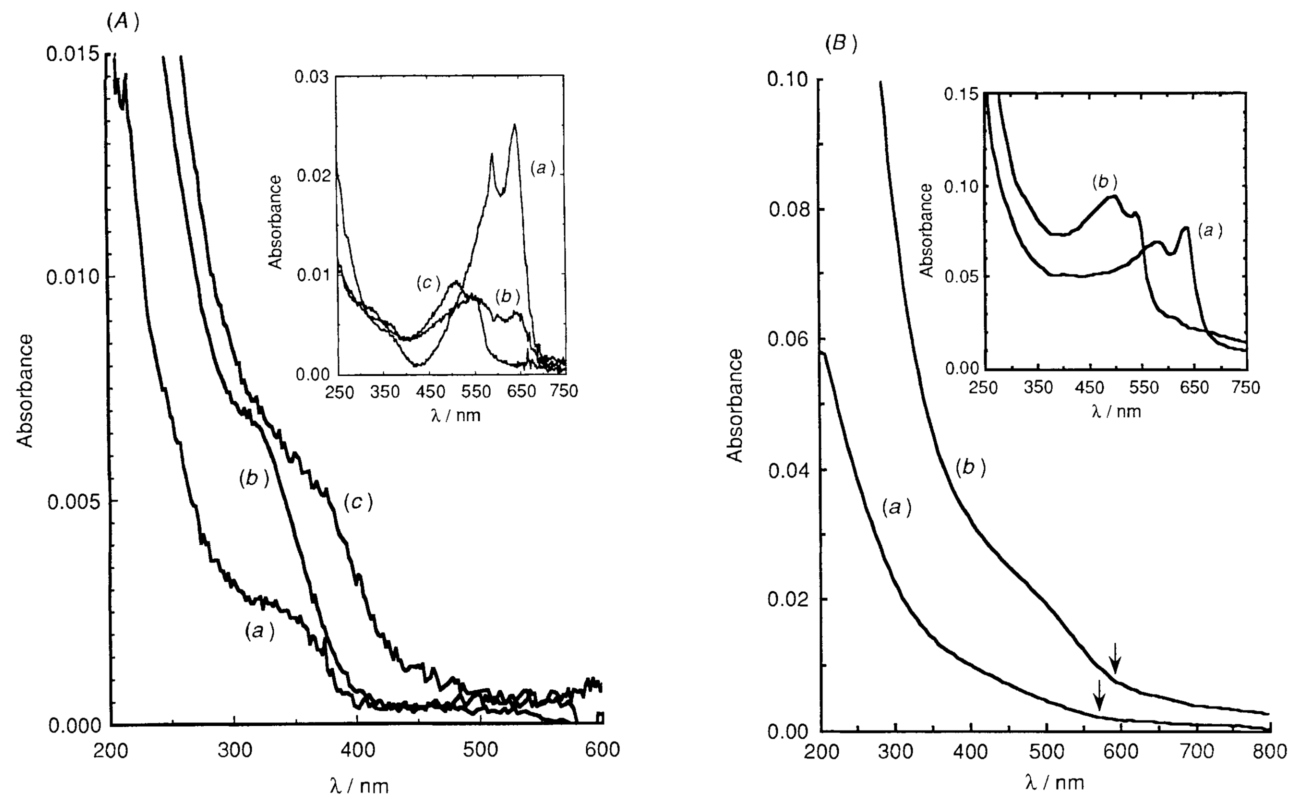

Fig. 2 (*A*): Absorption spectra of 19 layer films transferred at 20 mN m^{-1} and exposed to H_2S; (*a*) 75% DHP–25% 16–8 diynoic acid deposited from a subphase of $CaCl_2$ (10^{-3} mol dm^{-3}) and $CdCl_2$ (10^{-5} mol dm^{-3}; pH 9); (*b*) 50% DHP–50% 16–8 diynoic acid deposited from a subphase of $CaCl_2$ (10^{-3} mol dm^{-3}) and $CdCl_2$ (10^{-5} mol dm^{-3}; pH 9); (*c*) 25% DHP–75% 16–8 diynoic acid deposited from a subphase of $CaCl_2$ (10^{-3} mol dm^{-3}) and $CdCl_2$ (10^{-5} mol dm^{-3}; pH 9). Insert: spectra of multilayer films (*a*) and (*c*) after polymerization; (*a*) 25% DHP–75% 16–8 diynoic acid after 2 min UV irradiation; (*b*) 75%DHP–25% 16–8 diynoic acid after 2 min UV irradiation; (*c*) *b* after heating to 100 °C (5 min). (*B*): Absorption spectra of multilayer films transferred at 20 mN m^{-1} and exposed to H_2Se; (*a*) 1:1 DHP–16–8 mixed monolayer, deposited from a subphase of $CaCl_2$ (10^{-3} mol dm^{-3}) and $CdCl_2$ (10^{-5} mol dm^{-3}; pH 9) 9 layers; (*b*) 16–8 deposited from a subphase of $CdCl_2$ (10^{-3} mol dm^{-3}; pH 6.9), 7 layers. The arrows indicate the position of the bandgaps of the respective semiconductor particles. Insert: Spectra of cadmium 16–8 diynoic acid 3 layer films after polymerization; (*a*) after 2 min UV irradiation; (*b*) *a* after heating at 100 °C for 5 min.

diynoic acid polymer.[6] As far as we could tell there did not appear to be any spectral shift in the absorption of the colloid following the polymerization of the film.

The bandgaps of the three chalcogenides shown in Fig. 1 are 2.8. 2.1 and 1.7 eV for CdS, CdSe and CdTe, respectively. These energies can be compared to the bulk material values[7] of 2.4, 1.7 and 1.4 eV, for the same order, which clearly indicates that Q-state particles have been formed in the 16–8 diynoic acid films. For CdS and CdSe (which were examined in more detail than CdTe) the bandgap was found to be independent of the numbers of monolayers cast, at least up to 20 layers, indicating that the primary colloid is stabilized at a particular diameter (or narrow range) in the film. Bard and co-workers[8] obtained a similar result for CdS in cadmium arachidate films, and the bandgap was also the same as that found here in 16–8 films. Based on Henglein's[1] examination of the particle size–bandgap relationship for CdS, the CdS particles (if we assume they are spherical) in the 16–8 diynoic acid film are 4–5 nm in diameter. A similar size for the CdSe particles is suggested if we compare the absorption spectrum of CdSe in the film to that of the particles in acetonitrile.[9]

By altering the subphase conditions to pH 9 (NaOH) with $CdCl_2$ (10^{-5} mol dm^{-3}) and $CaCl_2$ (1–2 × 10^{-3} mol dm^{-3}) and using a mixture of 16–8 diynoic acid and dihexadecyl phosphate (DHP), even smaller particles of CdS and CdSe (not as pronounced a change as for CdS) could be produced in the LB films. This is shown by the spectra shift in the absorption curve seen in Fig. 2. It is important to point out that both the presence of Ca^{2+} (an inert ion diluent) in the subphase and DHP in the mixed monolayer are needed to shift the absorption spectrum to the blue. Polymerization of the mixed film still occurred (see insert in Fig. 2), with no obvious shift in the bandgap of the colloid. We do not yet know the reason why the presence of the DHP in the film results in the formation of the smaller colloids. A likely reason is that the DHP controls the domain size where particle nucleation–growth occurs as well as stabilizing a discrete size range depending on the amount of DHP in the film.

Additional control on the absorption spectrum of the chalcogenide could be achieved by the generation of mixed anion CdS_xSe_{1-x} particles, as shown in Fig. 3. The mixed anion Q-state particles were made by firstly generating CdS particles in a LB film, then exposing this film to H_2Se for 2–3 minutes. We assume that the thermodynamically favoured exchange of S^{2-} with Se^{2-} to yield mixed anion particles occurs quite rapidly because the primary CdS particles are of a size where *ca.* 50% of the CdS molecules making up the colloid are at the surface. Exposure of the CdSe particles in the films to H_2S, even after 1 hour, did not show any spectral changes due to displacement of Se^{2-} by S^{2-}. Recently, mixed anion CdS_xSe_{1-x} particles were generated in 'Nafion', with similar observations as reported here.[10]

Manipulation of the particle size and composition of the chalcogenide particles in polymerized diynoic acid films allows for the fabrication of a versatile nonlinear optical material. In addition, since polymerized diynoic acid films themselves can be used to generate 3rd and 2nd order nonlinear effects, depending on whether they are cast centrosymmetrically or

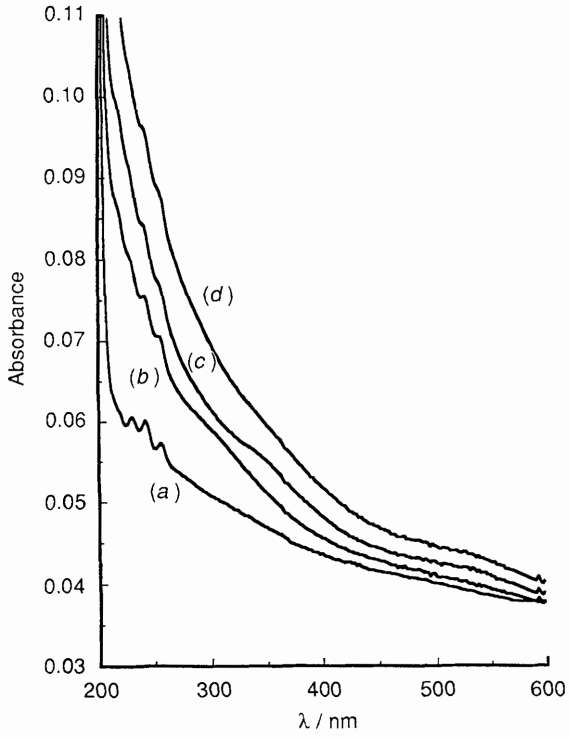

Fig. 3 Absorption spectra of; (*a*) 19 layer 16–8 diynoic acid films deposited from a subphase of $CdCl_2$ (10^{-3} mol dm^{-3}; pH 6.9) at 20 mN m^{-1} (background absorption); (*b*) after exposure to H_2S; (*c*) after exposure firstly to H_2S and secondly to H_2Se; (*d*) after exposure to H_2Se. The undulations in the absorption spectra in the range 220–260 nm are due to 16–8 diynoic acid monomer.

non-centrosymmetrically, the possibility exists for fabricating novel colloid-polymer films capable of simultaneously producing comparable 3rd and 2nd order nonlinear effects over a range of wavelengths.

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