The Fabrication of Titania Q-State Particles in Langmuir–Blodgett Films

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Optical absorption and XPS analyses have shown that titania Q-state particles (< 10 nm diameter) can be fabricated within arachidic (icosanoic) acid and cadmium arachidate Langmuir–Blodgett (LB) films by sequential exposure to gaseous titanium tetrachloride and water vapour; when a cadmium arachidate film was subsequently gassed with H_2S, sulfur was not incorporated into the film; CdS was not formed.

In recent years, there has been considerable research focus on the so-called Q-state particles; those with electrical and optical properties in between those of molecules and macroparticles.[1,2] Q-state properties are generally associated with particle diameters of less than 10 nm and the challenge has been to develop preparative procedures which generate particles in the desired size range. Such procedures have been greatly varied, involving both homogeneous[3] and heterogeneous[4,5] media; the latter include Langmuir–Blodgett films. It has been widely recognised that steric constrictions[6] and capping ligands[7] can provide meaningful control of particle size through restriction of growth. It remains unclear whether the high degree of molecular ordering characteristic of LB films plays a key role in the *in situ* nucleation and growth of particles.

Numerous types of Q-state particles have been prepared, the most popular being the chalcogenides like CdS,[1,8] PbS,[1] HgS[9] and CdSe.[10–12] Studies of TiO_2 nanoparticles have been few and seem restricted to polymer matrices[13] and reverse micelles.[14] This is a little surprising given the obvious interest in TiO_2 for new generation photoelectrochemical devices.[15] The present paper describes for the first time the fabrication of TiO_2 particles in Langmuir–Blodgett films. The films were constructed from arachidic acid and its cadmium salt.

Langmuir–Blodgett films of arachidic acid (ArH) and cadmium arachidate (CdAr) were deposited (at 20.0 ± 0.5 °C) using the vertical dipping technique onto hydrophobed quartz plates as previously described.[16] Precursor air–water monolayers were prepared by spreading a 3 mmol dm^{-3} solution of arachidic acid in $CHCl_3$ (Prolabo, spectroscopic grade) onto Milli-Q water (for ArH) or 0.4 mmol dm^{-3} $CdCl_2$ and 0.4 mmol dm^{-3} $KHCO_3$ (pH = 7.1) (for CdAr). The LB coated plates were exposed to $TiCl_4$ for 25 min in a dry nitrogen atmosphere in a 100 cm^3 sealed glass reaction vessel. One inlet port of the reaction vessel was connected to a supply of dry nitrogen while another was connected to a vessel containing liquid $TiCl_4$. The vessel containing $TiCl_4$ was connected to a supply of dry nitrogen so that the dry gas could be bubbled through the liquid. Flow through both inlet ports was controlled *via* glass taps. Before each exposure of the films to $TiCl_4$, dry nitrogen was allowed to flow through the reaction vessel for 10 min. The tap to the supply of nitrogen was then closed and the tap to the $TiCl_4$ source opened. Dry nitrogen was then bubbled through the $TiCl_4$ solution for 25 min. After reaction, the vessel was flushed again with dry nitrogen. Films were then removed from the reaction vessel and stored in air.

Fig. 1 shows the absorption spectra of TiO_2 within three different 20 layer LB films. Note, that all spectra presented in this paper have been corrected for absorbance due to the LB film itself. Negligible increases in absorbance occurred on $TiCl_4$ treatment unless the surfactant LB film was present. Two of the spectra in Fig. 1 show a characteristic absorption edge at *ca.* 340 nm, corresponding to a band-gap of 3.6 eV. The third film exhibited much less absorbance, with indication of more scattering and a much less defined band-gap absorption. XPS measurements of a film treated with $TiCl_4$ and then exposed to air showed a Ti/C mol ratio of 0.037 (see Table 1). This suggests near complete conversion (Ti/C = 0.05) of the arachidic acid molecules to $TiArCl_3$. Subsequent reaction with water vapour would then produce TiO_2, eqn. (1).

$$TiArCl_3 + 2\ H_2O \rightarrow TiO_2 + ArH + 3\ HCl \qquad (1)$$
$$Ar = Me[CH_2]_{18}CO_2$$

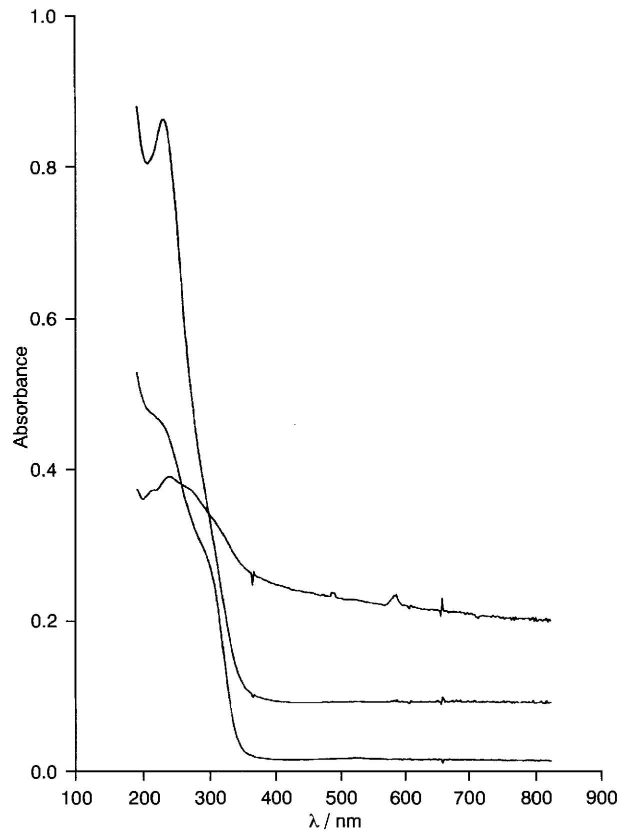

Fig. 1 Absorbance spectra of TiO_2 particles in 20 layer arachidic acid films; three separate experiments

Table 1 XPS data from Langmuir–Blodgett films (20 layers) treated with $TiCl_4$

	Mol ratios					
Film	Ti/C	O[a]/Ti	O[b]/C	Cl/Ti	Cl/Cd	S/Cd
Arachidic acid	0.037	1.7 (2)[c]	0.07 (0.1)	0.2	n/a	n/a
Cadmium arachidate treated with $TiCl_4$ and then gassed with H_2S	0.070 (1.0)	2.0 (2)	0.07 (0.1)	1.6	4.3	0.0

[a] Oxygen bound to titanium. [b] Oxygen bound to carbon. [c] Numbers in parentheses are those corresponding to reactions (1) to (3).

XPS measurements (Table 1) revealed stoichiometric formation of TiO_2.

We have not so far assessed the state of hydration in our films prior to their deliberate exposure to water vapour. Recent quartz crystal microbalance[17] and grazing angle FTIR studies indicate such hydration is likely to be low. Hence the formation of TiO_2 most probably occurs by diffusion of water vapour into the film. Note that the ratio of oxygen bound to carbon (Table 1) is close to that expected for arachidic acid whilst the chlorine to titanium mole ratio, at 0.2, is very much less than that corresponding to the reactant $TiCl_4$. This would indicate that the HCl mostly exists the film during hydrolysis of $TiCl_4$. The preparation conditions have not yet been consolidated with respect to the yield of TiO_2. The variations in Fig. 1 are probably due to incomplete reaction.

The absorption edge and band-gap of bulk TiO_2 are known[18] to be 380–400 nm/3.3–3.1 eV, depending on the crystal form. The blue shift seen in Fig. 1 (*ca.* 0.3–0.5 eV) shows clearly that Q-state particles have been formed. These particles must lie within the LB film. A band-gap of bulk TiO_2 would be expected for material precipated on the outer surfaces of the LB film. Similar blue shifts were found for 6, 10 and 20 layer films and have also reported for CdS and CdSe[6,14,18] fabricated within cadmium arachidate LB films.

Fig. 2 shows that Q-state TiO_2 particles can also be readily formed from LB films fabricated using the cadmium salt of arachidic acid. The particles exhibit a band-gap absorption at 360 nm; again a blue shift from the bulk TiO_2 bandgap of 380–400 nm.[18] Ti/C ratios from XPS measurements (Table 1) indicate the following reactions for $TiCl_4$ uptake and subsequent formation of particles (*i.e.* no water in the film) eqns. (2) and (3).

$$Ar_2Cd + 2\,TiCl_4 \rightarrow 2\,TiArCl_3 + CdCl_2 \qquad (2)$$

$$TiArCl_3 + 2\,H_2O \rightarrow ArH + TiO_2 + 3\,HCl \qquad (3)$$

The ratio of oxygen to carbon (Table 1) is again close to that expected for arachidic acid whilst the chlorine to titanium mol ratio, at 1.6, is again much less than that corresponding to the reactant $TiCl_4$. This is consistent with HCl exiting the film during hydrolysis of $TiCl_4$. The chlorine to cadmium ratio was much greater than that corresponding to $CdCl_2$ suggesting that not all the HCl has been lost from the film. The mol ratios of chlorine to titanium and cadmium indicate that *ca.* 20–23% of the HCl remained in the film.

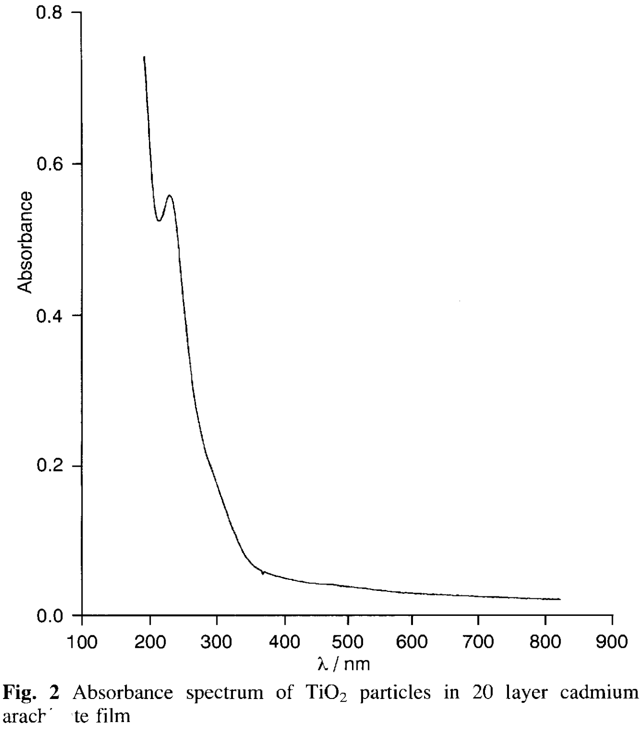

Fig. 2 Absorbance spectrum of TiO_2 particles in 20 layer cadmium arachidate film

In the treated CdAr films, TiO_2 particles would exist in the presence of $CdCl_2$. The form or location of this $CdCl_2$ has not yet been determined. Nevertheless, it was of interest to determine if this $CdCl_2$ could be reacted with H_2S, thereby producing two types of Q-state particle (TiO_2 and CdS) within the common organic LB matrix. Preliminary experiments have not been successful—gassing with H_2S for 20 min, sufficient time[16] for substantial conversion of an LB film of cadmium arachidate, produced no observable change in the absorption spectrum. XPS measurements (Table 1) reveal that sulfur was not incorporated into the film. This is indeed a perplexing result, as conversion of molecular $CdCl_2$ to molecular CdS (*i.e.* uptake of S) would have been expected even if the subsequent nucleation and growth of CdS particles was somehow retarded. It may be that nucleation of molecular $CdCl_2$ has formed particulates which show very little reactivity towards H_2S. It is likely that the reaction of H_2S with the particulates would be limited to just the outermost layer of Cd ions.[19,20]

This paper describes for the first time the fabrication of Q-state titania particles in Langmuir–Blodgett films. This opens up exciting new options for design flexibility in photoelectrochemical cells. Fabrication conditions are now being optimised by further study.

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