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Formation of TiO_2 nanoparticles in water-in-CO_2 microemulsions

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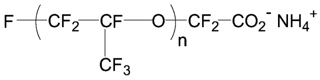
Titanium dioxide nanoparticles can be produced by the controlled hydrolysis of titanium tetraisopropoxide in water-in-CO_2 (w/c) microemulsions stabilized with the surfactants ammonium carboxylate perfluoropolyether (PFPE-NH_4) and poly(dimethyl amino ethyl methacrylate-*block*-1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate) (PDMAEMA-*b*-PFOMA); the greater control of hydrolysis and particle growth with PDMAEMA-*b*-PFOMA is consistent with the differences in the stabilities and interactions for these two microemulsions.

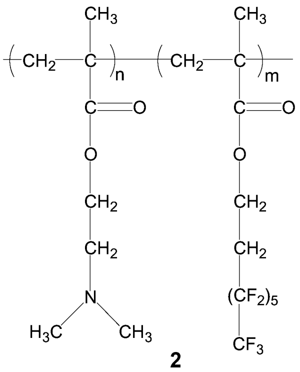
Water-in-oil (w/o) microemulsions have been utilized as templates to prepare TiO_2 nanoparticles,[1,2] which have attracted much attention as photocatalysts. The challenge has been to suppress uncontrolled particle aggregation in order to produce stable nanosized TiO_2 from titanium alkoxides which have very high reactivity toward water.[3–5] Here we report the use of w/c microemulsions to achieve particle size control for nanosized titanium dioxide.

Carbon dioxide is an attractive alternative to organic solvents because it is nontoxic, nonflammable, highly volatile, inexpensive, and environmentally benign. Water-in-CO_2 (w/c) microemulsions have been formed with especially designed surfactants containing 'CO_2-philic' fluorocarbon moieties.[6–9] In common with many w/o microemulsions, certain water-in-CO_2 (w/c) microemulsions exhibited a spherical droplet structure for which the droplet radius was directly proportional to the water-surfactant ratio, w_o.[9,10] Moreover they served as effective reaction vessels for inorganic,[11,12] organic,[13] and enzymatic reactions.[14] The objective of this work is to investigate the controlled formation of TiO_2 nanoparticles from direct reaction of titanium tetraisopropoxide (TTIP) with water solubilized in w/c microemulsions stabilized by low molecular weight and polymeric surfactants.

PFPE-NH_4 (M_w = 587) (**1**) was prepared by neutralizing PFPE-CO_2H with NH_3(aq). PDMAEMA$_{2K}$-*b*-PFOMA$_{10K}$ (**2**) was synthesized by sequential addition of DMAEMA and FOMA *via* group transfer polymerisation.† A stainless-steel view cell containing a sapphire window was used as a reaction vessel to prepare TiO_2 particles. The desired amount of surfactant and water were placed in a view cell and carbon dioxide was loaded at 3000 psi, 25 °C. For **2**, a stable single-phase w/c microemulsions were made after stirring the mixture for 30 min. For **1**, only part of the water was emulsified for the higher w_o values based on phase behavior measurements performed with a variable-volume view cell, which is described elsewhere.[13] Thus the interdroplet attractive interactions which limit microemulsion stability may be expected to be strong.[15] TTIP was then added to the w/c microemulsions and the pressure of the cell was raised to 4000 psi. After another 30 min of stirring, the product was collected after slowly venting CO_2. The particles were dried at 105 °C for 1 day and then calcined at 500 °C for 3 h. Table 1 summarizes the results of particle formation with different w_o values. In the case of w/c microemulsions formed with PDMAEMA$_{2K}$-*b*-PFOMA$_{10K}$, w_o represents the molar ratio of water to each DMAEMA unit in the PDMAEMA block ($[H_2O]/[DMAEMA]$) since the water only associates with the polar PDMAEMA groups of the polymer. For the hydrolysis of TTIP in the w/c microemulsion stabilized with **1**, the particles formed were unstable and precipitated in a few minutes after addition of TTIP. This instability became more pronounced as w_o increased. It appears that particle growth occurs within water droplets by rapid hydrolysis of TTIP and subsequent colloidal aggregation, which eventually leads to precipitates. The surfactant layer on the water core has limited ability to prevent aggregation. Attractive interdroplet interactions for the w/c microemulsions become stronger near the cloud point presssure. This pressure decreases with w_o.[15] In contrast, the TiO_2 particles produced by **2** were much more stable. For w_o below 10, the microemulsions were translucent after addition of TTIP without any appreciable precipitation, and the stability was maintained for 30 min. This greater stability and reduction in particle aggregation for **2** results in part from stronger steric stabilization due to the longer tails. Furthermore, the greater solvation of PFOMA *vs.* PFPE by CO_2[8] produces weaker intermicellar interactions.[15] and thus slower particle aggregation rates. At a high w_o, however, the flocculation rate of TiO_2 particles formed was high and a white precipitate was observed. The larger w_o produces stronger interdroplet interactions for the microemulsion resulting in particle flocculation. XRD measurement showed that as prepared particles were amorphous, while the particles calcined at 500 °C for 3 h were in the anatase form as depicted in Fig. 1.


$F-(CF_2-CF(CF_3)-O)_n-CF_2-CO_2^-\ NH_4^+$

1



2

Table 1 Nanosized TiO_2 powders[a] from hydrolysis of TTIP in w/c microemulsions stabilized by different surfactants

Surfactant	w_o	Observation	Crystallite size (XRD)[b]/nm	Crystallite size (TEM)/nm
1	5	Precipitate	12	12
	10	Precipitate	17	17
	20	Precipitate	18	19
2	5[c]	Translucent	9	8
	10[c]	Translucent	12	12
	20	Precipitate	17	18

[a] *R* ratio ($[H_2O]/[TTIP]$) = 2; [TTIP] = 0.11 mol dm^{-3}; calcination temperature = 500 °C. [b] Obtained from the Scherrer equation. [c] [TTIP] = 0.06 mol dm^{-3}.

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The crystallite size of the particles determined by the Scherrer equation from XRD patterns are listed in Table 1. The crystallite size increases (from 12 to 18 nm) with an increase in w_o from 5 to 20 in the w/c microemulsion based on **1**. A similar trend was also observed for **2**. Thus the crystallite size prepared by the microemulsion method can be controlled by w_o which affects the water pool size and interdroplet interactions. TEM was used to investigate the exact microstructure of the particles as shown in Fig. 2. The size of crystallites correspond closely to the sizes from XRD analysis (Table 1). The uniform 12 nm particles in the TEM photograph of the sample produced by **1** are highly aggregated. The particles produced by **2** are much less aggregated, with aggregation numbers from 5 to 50. Some non-aggregated particles with an average diameter of *ca.* 4 nm are also observed as labeled with arrows in Fig. 2B. Hence it is obvious that **2** can suppress the aggregation of TiO_2 particles much more effectively than **1**.

For most cases, the average diameters of TiO_2 particles after calcination are larger than normal micellar diameter. The water core size of w/c microemulsions stabilized PFPE-NH_4 ([PFPE] = 2.1 wt%, w_o = 11) at 35 °C was measured to be approximately 4 nm by small angle neutron scattering.[10] However the diameter of calcined TiO_2 which was produced by **1** at w_o of 5 was 12 nm, indicating growth during intermicellar collisions.[16] Another factor for this difference is grain growth during the calcination at high temperature.[17] In conclusion, TiO_2 nanoparticles have been produced by the controlled hydrolysis of TTIP in the w/c microemulsions stabilized by low molecular weight and polymeric surfactants. The crysrallite size can be controlled by the water-to-surfactant mole ratio w_o which influences the hydrolysis rate, droplet size and intermicellar interactions. The particle aggregation was reduced remarkably by **2** which formed more stable microemulsions with weaker interdroplet interactions due to the longer length and stronger solvation of PFOMA *vs.* PFPE.

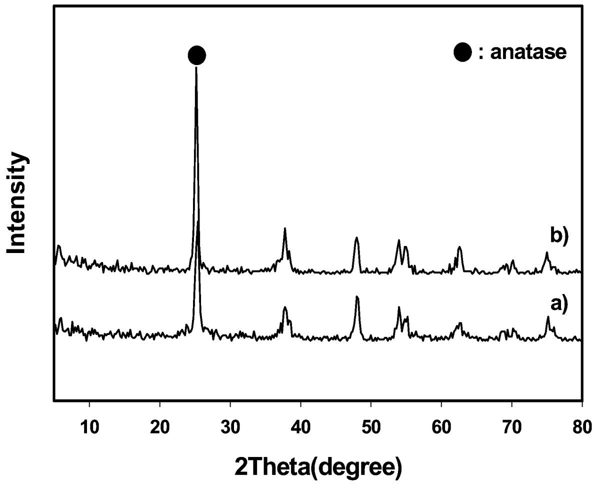

Fig. 1 XRD patterns of nanosized TiO_2 powders prepared by different surfactants at w_o = 20, R = 2 and calcined at 500 °C: (a) **1** and (b) **2**.

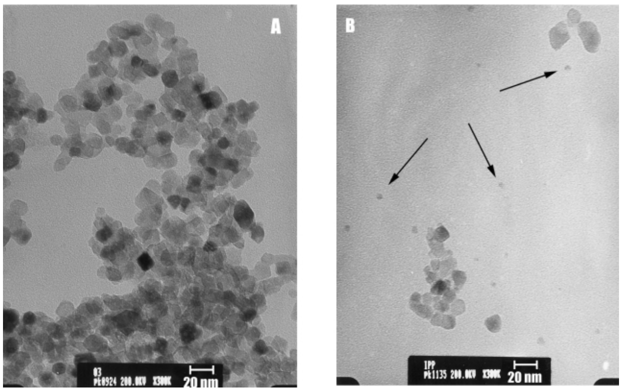

Fig. 2 TEM micrographs of TiO_2 particles obtained by hydrolysis of TTIP in w/c microemulsions stabilized by (A) **1** and (B) **2**, and calcined at 500 °C for 3 h.

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Notes and references

† *Synthesis* of PDMAEMA-*b*-PFOMA: the group transfer polymerisation was carried out under argon atmosphere in a previously flamed glass reactor. 15 mL of THF and 10 mg (0.02 mmol) of tetrabutylammonium bibenzoate were transferred into a reactor by means of a cannula. Then 0.174 g (1.0 mmol) of methyl trimethylsilyl dimethylketene acetal was added to the mixture *via* syringe. After 5 min of stirring, 1.8 g (11.5 mmol) of freshly distilled DMAEMA was added slowly *via* syringe and the polymerisation proceeded for an hour under argon. The GPC analysis of an aliquot showed M_w/M_n = 1.11. For the block copolymerization, 5.5 g (12.7 mmol) of freshly distilled 1*H*,1*H*,2*H*,2*H*-FOMA was added to the living PDMAEMA solution. The mixture was stirred for additional hour and quenched with degassed methanol (2 mL). THF and methanol were removed by evaporation and a possible DMAEMA homopolymer was extracted with hexane. The product was collected, dried, and weighed to give 5.9 g of polymer. The molecular weights of PDMAEMA and PFOMA block of the copolymer were determined to be 2000 and 10000 by ^1H NMR analysis, respectively.

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