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CoMo GROUP

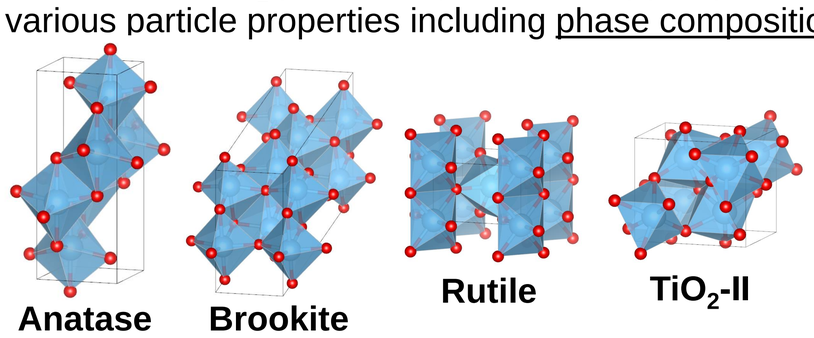
C4T

Polymorphism of nanocrystalline TiO_2 prepared in a stagnation flame: Formation of TiO_2-II phase

A metastable "high-pressure" phase TiO_2-II is prepared using a laminar premixed stagnation flame. The formation of TiO_2-II in an atmospheric pressure flame is hypothesised to be kinetically driven through the oxidation and/or solid-state transformation of a sub-oxide/pre-rutile intermediate.

1 INTRODUCTION

Performance of TiO_2 photocatalysts is strongly dependent on various particle properties including phase composition.



The aim is to understand how these different crystal structures are formed during the nanoparticle synthesis.

2 NANOCRYSTALLINE TiO_2 SYNTHESIS

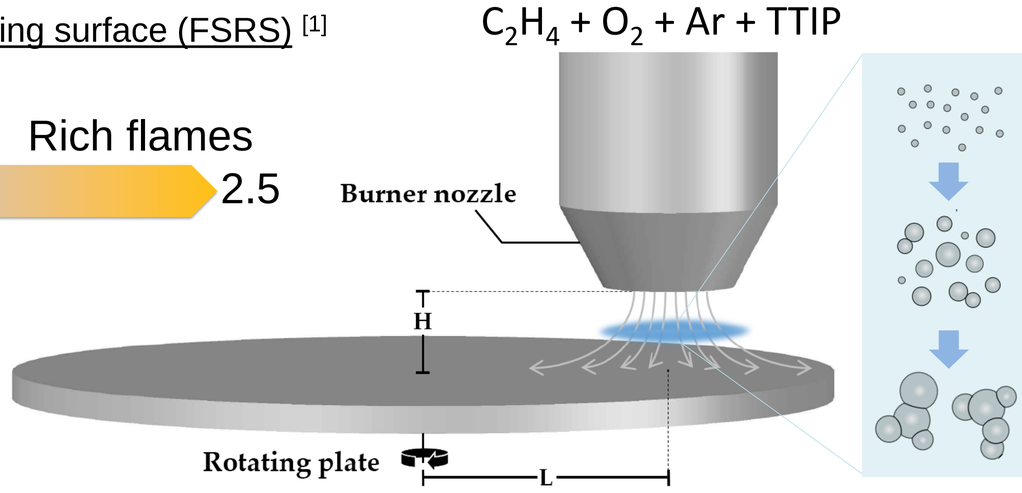
Flame stabilised on rotating surface (FSRS) [1]

Lean flames — Rich flames

0.3 — 1.0 — 2.5

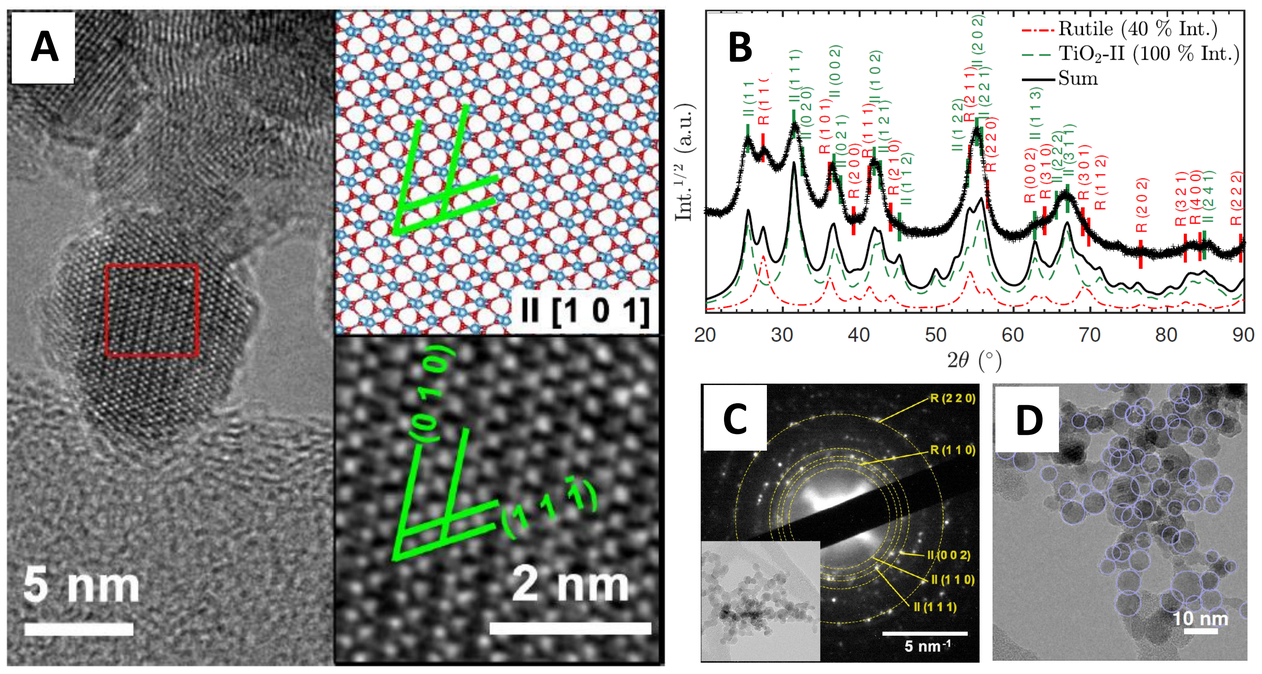
$$\phi = 3\frac{X_{C_2H_4}}{X_{O_2}}$$

ϕ = Equivalence ratio



3 MATERIALS CHARACTERISATIONS

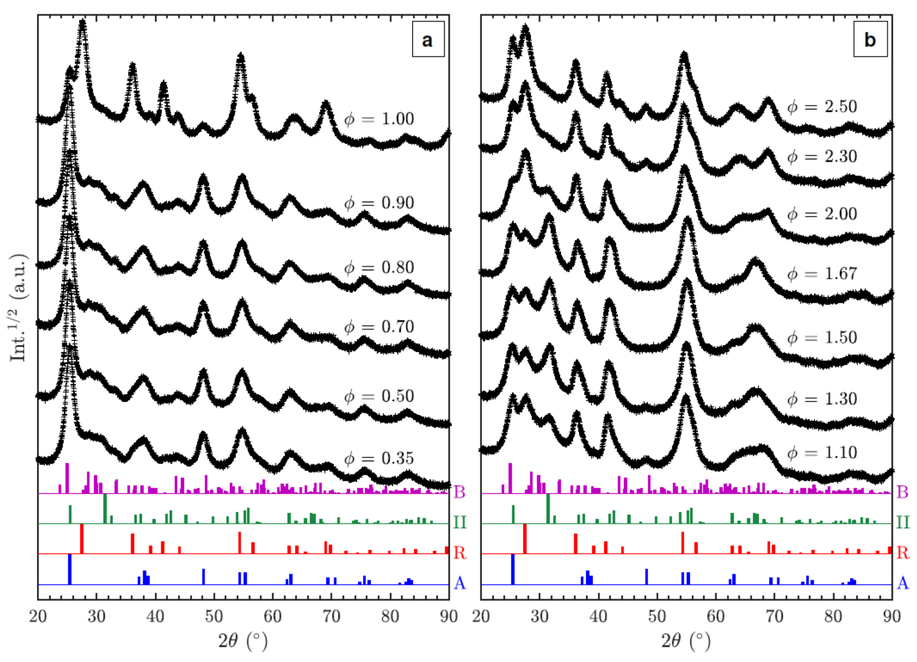
The synthesised nanoparticles were characterised and four distinct polymorphs were identified.



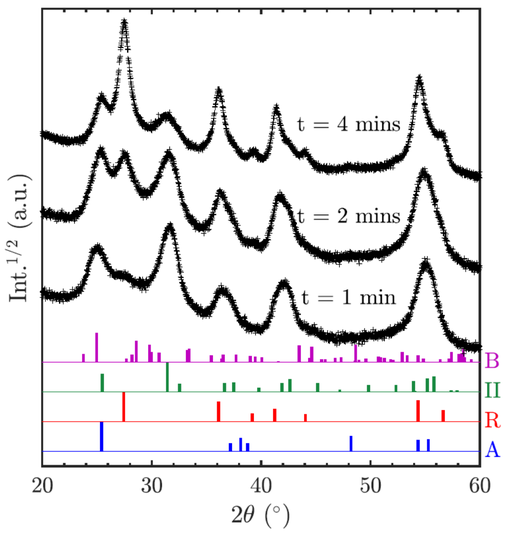
A: An HRTEM image showing a TiO_2-II polymorph with the corresponding structural model;
B: Powder XRD, and **C**: SAED patterns showing rutile/TiO_2-II mixture – with possible anisotropy;
D: A TEM image showing nearly spherical particles with size ~9 nm (ϕ = 1.67).

4 EFFECTS OF FLAME EQUIVALENCE RATIO/DEPOSITION TIME

Mixtures of anatase/brookite and rutile/TiO_2-II were formed predominantly in lean and rich flames, respectively. The transition occurs at around ϕ = 1.0.



XRD patterns of samples collected at varying equivalence ratio (ϕ) with rotating stagnation plate.



XRD patterns of samples collected at varying deposition time with non-rotating stagnation plate (ϕ = 1.67).

5 DISCUSSION

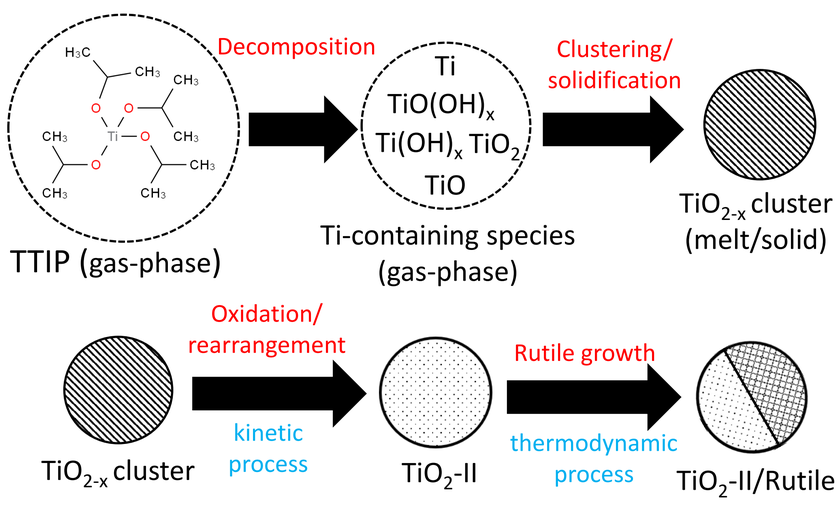
Formation of TiO_2-II is only thermodynamically favourable at very high pressure.

Other ambient pressure syntheses of TiO_2-II suggest that TiO_2-II is formed preferentially at oxygen-lean environments, for example:

- In atomic layer deposition (ALD) experiments as a mixture with rutile showing strong anisotropy. [2]
- As a product of α-Ti_3O_5 oxidation with boiling sulphuric acid. [3]

6 CONCLUSIONS

It is hypothesised that TiO_2-II is formed as a pre-rutile phase through solid-state transformation of a sub-oxide intermediate.



Mixtures containing three-phase heterojunctions are potentially important in photocatalysis due to enhanced electron-hole separation. [4]

7 KEY REFERENCES

[1] E. D. Tolmachoff, A. D. Abid, D. J. Phares, C. S. Campbell and H. Wang, *Proc. Combust. Inst.*, 2009, **32 II**, 1839–1845.
[2] J. Aarik, Philos. *Mag. Lett.*, 1996, **73**, 115–119.
[3] I. E. Grey, C. Li, I. C. Madsen and G. Braunshausen, *Mater. Res. Bull.*, 1988, **23**, 743–753.
[4] W.-N. Zhao, S.-C. Zhu, Y.-F. Li and Z.-P. Liu, *Chem. Sci.*, 2015, **6**, 3483–3494.

Acknowledgements CREATE

This project is supported by the National Research Foundation, Prime Minister's Office, Singapore under its CREATE programme.

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