CONTROLLED SYNTHESIS OF HIGHLY-CRYSTALLIZED ANATASE AND RUTILE TiO_2 NANOCRYSTALLITES

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Anatase TiO_2 has large band gap energy and suitable redox potentials for practical use in photocatalysis and photoelectronics. Rutile TiO_2 exhibits higher thermal stability than anatase and brookite TiO_2, and has the band gap energy and potentials of conduction and valence bands similar to anatase. Research on rutile TiO_2 nanocrystallites has not well been developed because synthesis of pure rutile nanocrystallites with controlled size and crystal shape is still difficult. We present synthesis methods for selective preparation of nanosized phase-pure anatase and rutile TiO_2 using amorphous TiO_2 as a starting material and acids such as hydrofluoric, hydrochloric, nitric, and citric acids as catalysts (Scheme 1). Well-dispersed anatase and rutile nanocrystallites were simply prepared. The sample preparation conditions are listed in Tables 1 and 2.

The powder XRD and HRTEM measurements showed that samples A5, A8, and A12 were phase-pure nanosized anatase TiO_2 with narrow particle size distribution ranging from 3 to 20 nm. The presence of HF and another acid, i.e., HCl or HNO_3, as a cooperative acid catalyst enhanced crystallization of anatase from amorphous during the hydrothermal processing. The average particle sizes of the sample A5, A8, and A12 were 9, 12.8, and 12.3 nm, respectively. A5 and A8 samples were of regular crystal surfaces, but the crystal surface of A12 was irregular.

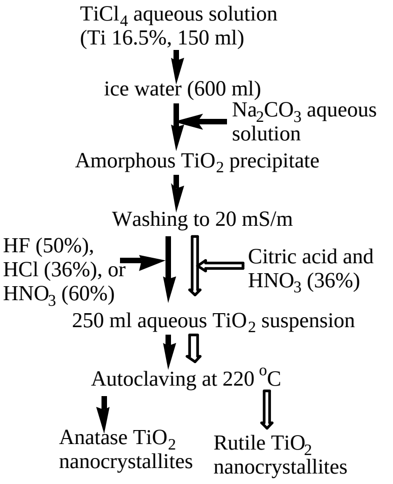
Well-dispersed rod-like rutile nanocrystallites (R3) with average sizes of 12.1 by 30.5 nm in width and length were prepared using citric and nitric acids as catalysts by autoclaving amorphous TiO_2 aqueous suspension at pH 1.09 and 150 °C for 22 h. When the pH value was decreased to 0.8, the particle sizes were increased to 14.8 by 53.2 nm (R2). The particle sizes were increased to 31.9 by 72.5 nm when the autoclaving was carried out at 220 °C for 13 h (R7). The nanocrystallite sizes were increased by lowering the pH value and increasing the autoclaving temperature.

The crystallization processes of anatase and rutile TiO_2 are postulated in Scheme 2.

Protonation of amorphous TiO_2 with acids leads to the phase-pure formation of anatase TiO_2 nanocrystallites. Chelation and protonation of amorphous TiO_2 result in the formation of phase-pure rutile TiO_2 nanocrystallites.

REFERENCES

(1) H. Yin, Y. Wada, T. Kitamura, and S. Yanagida, *J. Mater. Chem.* 11, 1694, 2001.



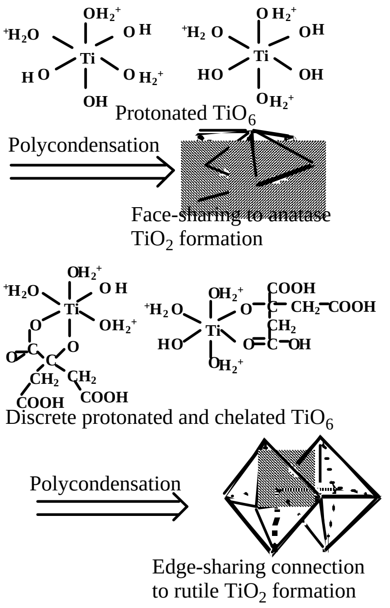
Scheme 1. Hydrothermal synthesis processes of anatase and rutile TiO_2 nanocrysatllites from amorphous phase.

Table 1. Preparation conditions of nanosized anatase TiO_2.

Samples	HF (M)	HCl (M)	HNO_3 (M)	Autoclaving time (220°C)/h
A5	0.12	1.38		2
A8	0.12	1.38		4
A12	0.12		1.58	4

Table 2. Preparation conditions of nanosized rutile TiO_2.

Samples	pH	Autoclaving	
		Temp./°C	Time/h
R2	0.8	150	22
R3	1.09	150	22
R7	0.8	220	13



Scheme 2. Crystallization of anatase and rutile TiO_2 from amorphous phase catalyzed by acids.