

Aerosol-assisted processing of colloidal TiO₂ nanoparticles

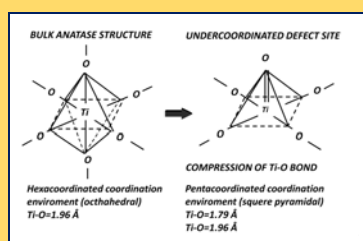
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MOTIVATION

It is well known when nano-crystalline TiO₂ becomes smaller than 20 nm Ti atoms which are located near the surface of the particles (for 5nm particles ~40% of Ti atoms are located at the particle surface) change their environment from six-coordinated (octahedral) to five-coordinated (square pyramidal).^[1] Because of spherical geometry and large curvature of small particles surface states become under-coordinated defect sites more capable for binding enediol ligands. In the relation between under-coordinated defect sites and surface modifiers, coordination of Ti atoms returns back into its initial six-coordinated environment.



Do we have the opportunity to synthesize submicron particles that have nanometer size regime properties?

In this research we will try to find the answer by processing of colloidal TiO₂ nanoparticles using aerosol-assisted self-assembly method.

ABSTRACT

Highly spherical, submicronic assemblage of TiO₂ particles were prepared by ultrasonic spray drying/pyrolysis of aqueous colloidal TiO₂ (~ 4.5 nm) precursor solution in a wide temperature regime (150-800 °C).

The obtained spherical particles (assemblage of primary nanoparticles), were additionally modified, with some different surface active ligands (ascorbic acid, dopamine, catechol, 2,3-dihydroxynaphthalene and anthrabin).

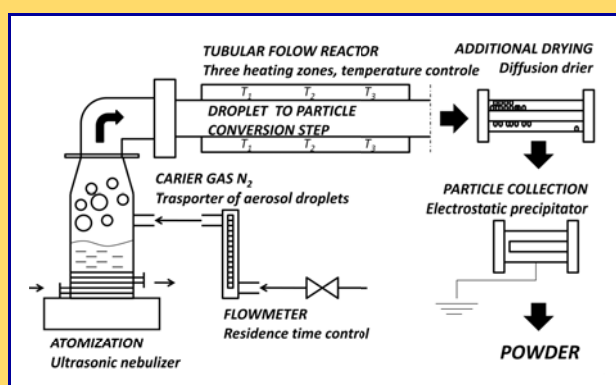
For all TiO₂/L powders extensive red shift in reflection spectra is observed in comparison to the bare TiO₂ particles, E_g ~ 3.2 eV. This significant band gap change was assigned to the high reactive centers Ti atoms at the surface TiO₂ nanocrystallites (~ 4.5 nm) which are pentacoordinated (square pyramidal).

The formation of charge transfer (CT) complexes on ligand-modified TiO₂ and their binding structures were investigated by using FTIR spectroscopy.

PROCESSING

In attempt to select a method that involves only the process of evaporation and self-assembly of colloidal solution nanoparticles inside the droplet, spray-pyrolysis/drying method is imposed as a logical solution. Also, the method provides easy control over morphology and phase composition of nano-structured particles simply adjusting process parameters such as: residence time of droplets (flow rate of carrier gas), hot wall temperature (heating rate of droplets) and concentration of starting solution. The process consists three interrelated regions in line.

Detailed description of process includes colloidal solution atomization, droplet to particle conversion and particle collection, as schematically shown in the picture.

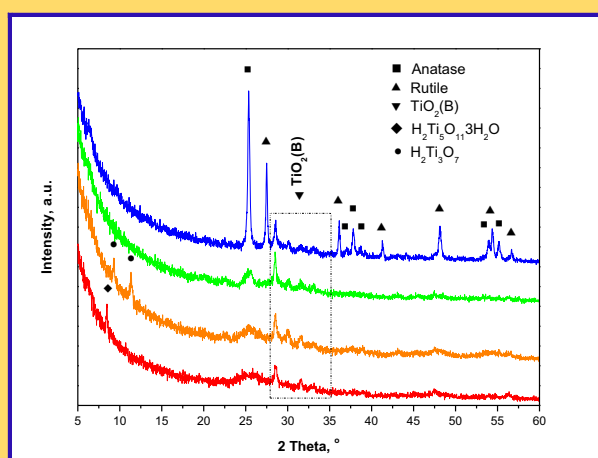


Diversity and potentials of the aerosol route for making functional materials at the nano size level are described in detail in literature.^[2]

RESULTS

Structural refinement was performed through combined Rietveld and Le Bail analyses using Topas Academic software.

As processing temperatures increases the crystal size increases as well and obtained powders crystallizes in anatase and metastable form of TiO₂(B) phase, except for powder obtained at 800°C where 30% anatase transforms to rutile phase.

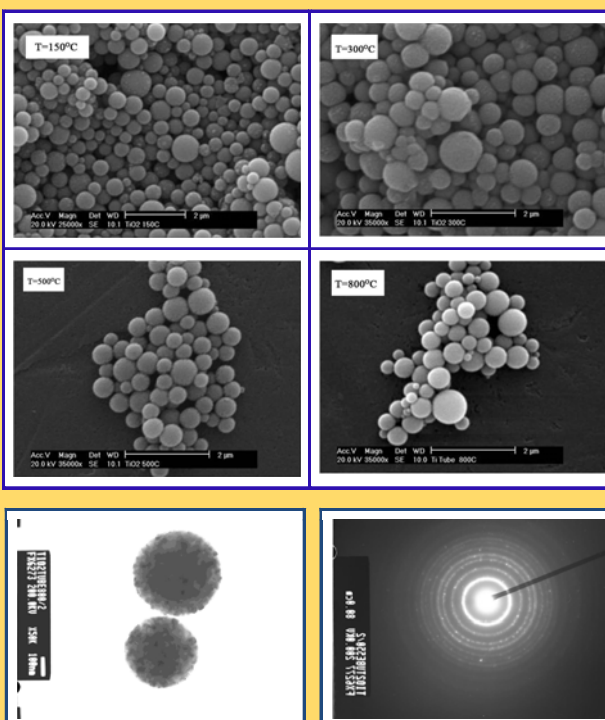


T, °C	Crystal structure	System	Space group	Lattice constants, nm			CS, nm
				a	b	c	
150	TiO ₂ anatase	Tetragonal	I4 ₁ /amd	0.376	-	0.950	2.5
	TiO ₂ (B)	Monoclinic	C2/m	0.122	0.372	0.652	
	H ₂ Ti ₃ O ₇ ·3H ₂ O	Monoclinic	C2/m				
300	TiO ₂ anatase	Tetragonal	I4 ₁ /amd	0.376	-	0.950	9
	TiO ₂ (B)	Monoclinic	C2/m	0.122	0.372	0.652	
	H ₂ Ti ₃ O ₇	Monoclinic	V2/m	0.160	0.374	0.921	
500	TiO ₂ anatase	Tetragonal	I4 ₁ /amd	0.376	-	0.950	21
	TiO ₂ (B)	Monoclinic	C2/m	0.122	0.372	0.652	
	TiO ₂ rutile	Tetragonal	P4 ₂ /mnm	0.459	0.296		
800	TiO ₂ anatase	Tetragonal	I4 ₁ /amd	0.376	-	0.950	53
	TiO ₂ rutile	Tetragonal	P4 ₂ /mnm	0.459	0.296		
	TiO ₂ (B)	Monoclinic	C2/m	0.122	0.372	0.652	

X-ray powder diffraction reference patterns:
 Crystal structure PDF card numbers
 TiO₂ anatase PDF 89-4921
 TiO₂ (B) PDF 74-1940
 TiO₂ rutile PDF 89-4920
 H₂Ti₃O₇·3H₂O PDF 44-0130
 H₂Ti₃O₇ PDF 47-0561

SEM analysis shows that all particles have spherical morphology, narrow particle size distribution and self-assembled structure. As processing temperature increases from 150 to 800°C, the mean diameter decreases from 438 to 345 nm.

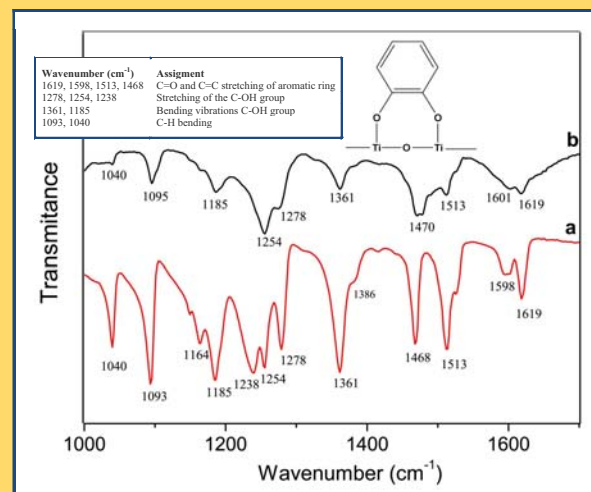
At low temperature solvent evaporation rate is low, primary nanoparticles make aggregation into a spherical, soft, nano-porous assemblage- so called "secondary particle". At higher temperatures the collision and aggregation of primary particles is more pronounced and it resulting in decreasing mean size of secondary particles.



SEM and TEM images of TiO₂ particles with the corresponding SAED pattern.

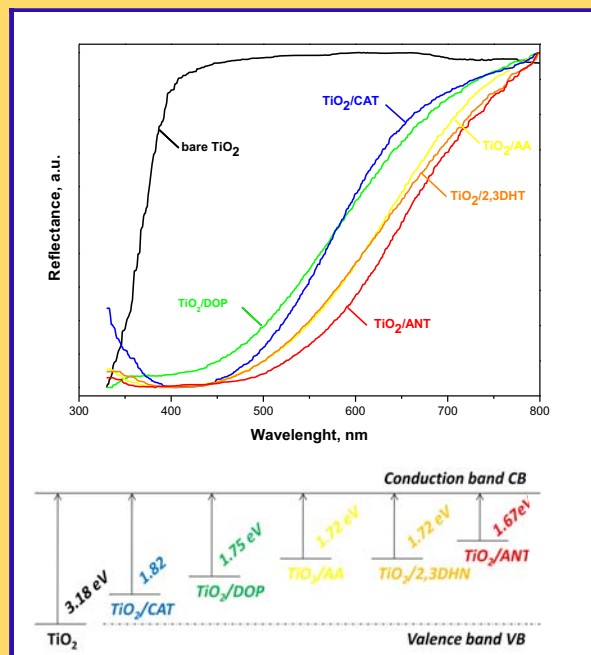
The FTIR spectra (1700-1000cm⁻¹) of catechol (a) and catechol adsorbed on submicron TiO₂ particles (b), with proposed binding structure, are shown in the next figure, while assignment of IR absorption bands of free catechol is shown into table.

The difference between FTIR spectra of free catechol and catechol adsorbed on the surface of TiO₂ particles appears, indicating surface complexation with catechol bound to oxide surface in bidentate form.



The effective band gap value for ligand-TiO₂ modified system was estimated from the Kubelka-Munk function.

$$f(R) = \frac{K}{S} = \frac{(1-R)^2}{2R}$$



The effective band gap energies of TiO₂/L (L=CAT, DOP, AA, 2,3DHN and ANT) particles were calculated by Kubelka-Munk function to be 1.82, 1.75, 1.72, 1.72, and 1.67 eV, respectively. Red shift in reflection spectra is observed in comparison to the bare TiO₂ particles, E_g ~3.18eV.

CONCLUSION

By applying of aerosol assisted self-assembly method it is possible to retain the properties of nanoparticles in the frame of submicron TiO₂ spheres with controlled phase composition, particle size distribution and properties of the outer surface of the particles.

All used modifiers form a charge transfer complex on the surface of the submicron TiO₂ particles resulting in change of their optical properties, that have been insighted so far only for the individual nanoparticles.

REFERENCES

- (1) Rajh, T.; Nedeljkovic, J. M.; Chen, L. X.; Poluektov, O.; Thurnauer, M. C. *J. Phys. Chem. B* **103** (1999) 3515.
- (2) O.Milosevic, L.Mancic, M.E. Rabanal, L.S.Gomez, K.Marinkovic, *KONA Powder and Particle Journal* **27** (2009) 84-106.