

On the Morphologies and Photocatalytic Properties of TiO₂ Nanoparticles Synthesized by Pulsed-Laser Decomposition of Titanium Tetraisopropoxide

M. Mozael¹, Z. Dong¹, S.D. Tse¹, B.H. Kear² and J. F. Al-Sharab³

¹ Department of Mechanical and Aerospace Engineering, Rutgers University, Piscataway, NJ, USA

² Department of Materials Science and Engineering, Rutgers University, Piscataway, NJ, USA

³ Department of Engineering Technology, Northwestern State University, Natchitoches, LA, USA

Titanium dioxide belongs to the transition-metal oxide family and forms several polymorphs, including anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). In comparison with other polymorphs, anatase-TiO₂ is preferable for solar cell applications because of its high electron mobility, low dielectric constant, and low density [1,2]. In this investigation, a novel method is used to synthesize amorphous TiO₂ nanoparticles, which upon subsequent post-annealing transform into unique nanostructures of anatase-TiO₂. The resulting nanostructures display photocatalytic activity, which is enhanced when the anatase-TiO₂ is doped with W using this new synthesis method.

The new method to synthesize amorphous-TiO₂ nanoparticles involves pulsed-laser decomposition of titanium tetra-isopropoxide (TTIP). In practice, the laser is focused just below the surface of the liquid-TTIP precursor, forming a high enthalpy *submerged-plasma* where rapid precursor decomposition occurs, generating vaporized species that upon subsequent rapid condensation and quenching by the surrounding liquid precursor yield nanoparticles of amorphous-TiO₂. Upon post-annealing at 400°C for 2 hours, nanoparticles of amorphous-TiO₂ undergo a phase transition to anatase-TiO₂, with essentially no change in particle size. Upon post-annealing at 800°C, anatase-TiO₂ undergoes a phase transition to rutile-TiO₂, Figure 1.

Examination of anatase-TiO₂ nanoparticles by high resolution electron microscopy shows partially- or fully-transformed nanoparticles. Lattice imaging of a typical *fully-transformed spherical-shaped TiO₂ nanoparticle* reveals a radially-symmetric nanograin structure, in which each nanograin is separated from its neighbor by a disordered region that contains a high density of lattice defects. Furthermore, lattice imaging of a typical *partially-transformed spherical nanoparticle* reveals a core-shell structure, in which the shell consists of fully-transformed (crystalline) anatase-TiO₂, and the core consists of untransformed amorphous-TiO₂, Figure 2(a). It is concluded that the amorphous-to-anatase phase transformation starts at the surface of a nanoparticle, irrespective of its morphology, and propagates into the interior by a diffusion-controlled mechanism, possibly involving counter-diffusion of O and C species. In one case, Figure 2(b), such a diffusion-controlled transformation into anatase TiO₂ in a partially-transformed nanofiber appears to occur by incremental propagation in a *layer-by-layer* manner. Details of these phase transitions and the resulting nanopowder products will be described, as well as their photocatalytic properties, including the effects of W-doping of the anatase-TiO₂ nanoparticles.

References:

[1] Liu, Nan *et al*, Catalysis Today **225** (2014), p. 34.

[2] Carp, Oana, Carolien L. Huisman, and Armin Reller. *Progress in Solid State Chemistry* **32.1** (2004), p. 33.

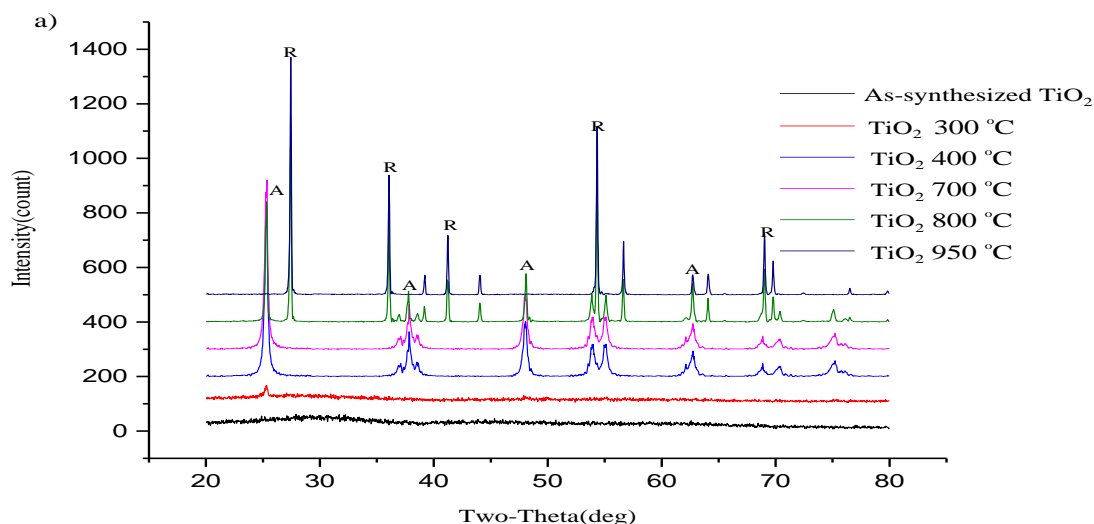


Figure 1. A series of XRD spectra for as-synthesized amorphous-TiO₂ nanoparticles, after post annealing at 300-950°C for 2 hr in air, showing transformation to anatase-TiO₂ at ~ 400°C, and then to rutile-TiO₂ at ~ 800°C. (A-anatase-97-004-4882, R-rutile-97-000-9161).

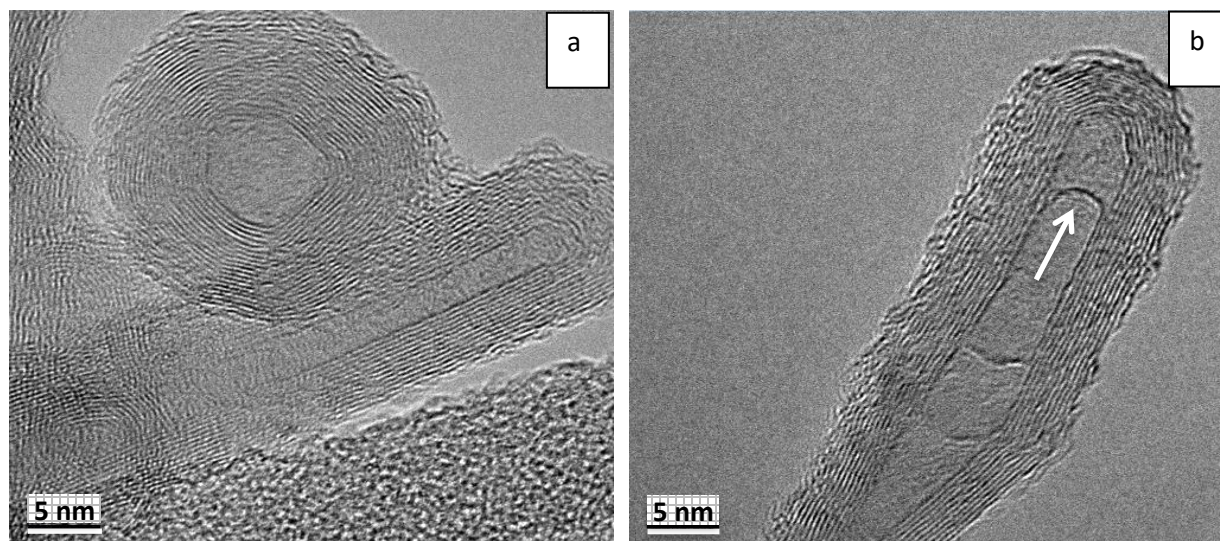


Figure 2. As-synthesized amorphous-TiO₂ nanoparticles after annealing at 400°C for 2 hours showing: (a) core-shell structures of partially-transformed nanoparticles, in which the shell is transformed (crystalline) anatase-TiO₂ and the core is un-transformed amorphous-TiO₂; and (b) high resolution image of a nano-fiber indicating propagation of a phase-transformation interface via a layer-by-layer mechanism (note propagation of a single molecular layer indicated by the arrow).