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Structural Analysis of Flame Synthesized C-Doped TiO_2 Nanocomposite Polymorphs for Energy Related Applications

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Titania, TiO_2 is well-known material with many different industrial applications due its low cost, chemical inertness, eco-friendly nature, physical, mechanical, optical and electrical properties. TiO_2 exhibits many polymorphs at ambient as well as high pressure/temperature conditions. Synthesis of nano-TiO_2 particles and composites is receiving a great attention in many energy related applications such as energy harvesting (solar cells), energy storage (batteries), photocatalysis, and water splitting. The efficiency of TiO_2-based devices depends on the crystal structure as well as chemical compositions of the TiO_2-nanocomposite at the atomic scale. However, detailed structural analysis of nanostructured materials (<10 nm) is challenging and requires high quality diffraction data using synchrotron X-ray or spallation neutron sources. In this paper, we describe flame synthesis and structural analysis of C-doped TiO_2 polymorphs utilizing a flat-flame burner of novel design, which is capable of continuous operation at reduced pressures. Detailed structural and chemical characterization using TEM and selected area electron diffraction (SAED) will be presented. In addition, in order to obtain quantitative structural analysis of the doped-TiO_2 polymorphs synthesized in this study, samples will be analyzed using electron pair distribution functions (ePDFS), a new emerging powerful tool recently developed [1].

The synthesis of C-doped TiO_2 powders was carried out in the flat-flame burner, using titanium-isopropoxide as the precursor material. After thermal decomposition and vapor condensation, the resulting nanopowders were collected on achilled substrate. Methane gas was used as a source of carbon doping. Carrier gas flow rate was adjusted to control the amount of dopant in the TiO_2 nanoparticles. *In-situ* laser diagnostics techniques were used to determine chemistry of gas-phase species and to detect any phase transformation that occursduring deposition. With this novel design, various C-TiO_2 nanocomposite polymorphs including, anatase, brookite, rutile were synthesized. In addition, srilankite, a high-pressure phase which is hardly accessible with others techniques, was stabilized at ambient conditions. Furthermore, accurate control of process parameters of the flat-burner system allows synthesis of nanocomposites with controlled amounts of carbon and oxygen.

Fig. 1-a shows a bright-field TEM image, and corresponding SAED of as-synthesized C-TiO_2 nanocomposite. The average particle size is 8nm with a narrow particle size distribution ±0.9 nm. Indexed rings of SAED, **Fig. 1-b** shows a close match with of anatase phase and diffuse rings is indicative of nano-sized particles. EELS and EDS chemical analyses show that the sample contains a ~7-15 (%wt.) carbon, **Fig. 2**. Standard testing of fabricated DSSCs of the C-TiO_2 anatase powder, showed an increase in visible light absorption, which resulted in ~17% increase in the photocurrent

density, and ~23% overall increase in the efficiency with respect to photoanodes made from commercially available anatase Degussa P-25 TiO_2 [2]. The improvement in the photocatalytic activity my be due to the increase in the number of absorption sites and shift in the band gap [3]. Work is underway to determine the location of the carbon atoms in the TiO_2 structure, and their role in photocatalytic activity. Detailed refinement analysis using ePDFs will be employed to extract quantitative structural information about the local structure in the doped-TiO_2 nanocomposites. Combining ePDFs structural analysis with sub-nanometer EELS compositional mapping will accurately allow correlating structure with properties of the synthesized TiO_2 polymorphs nanocomposites.

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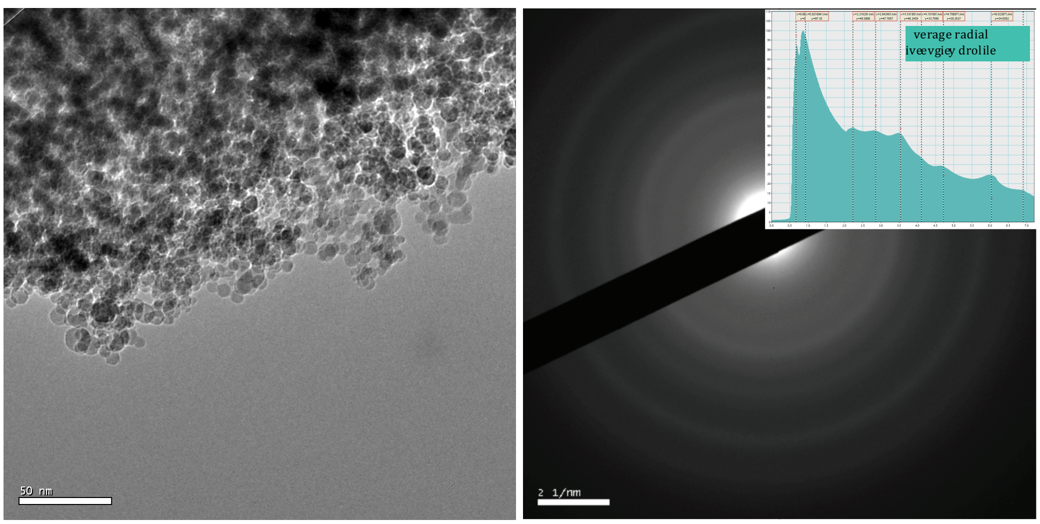
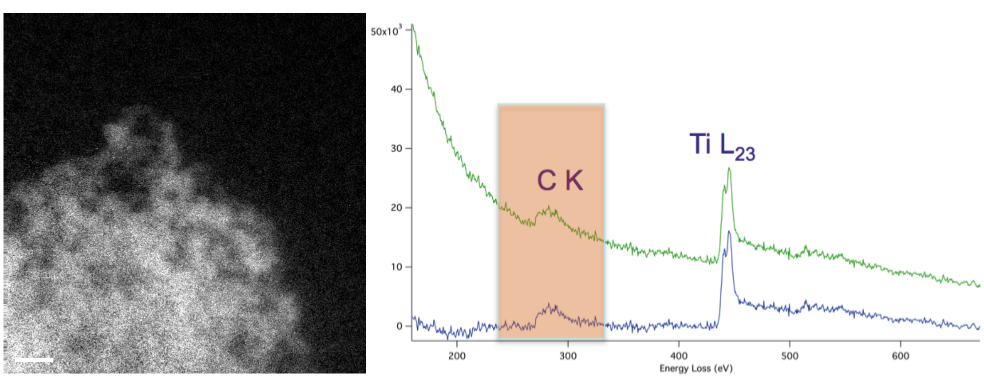


(a) (b)

Figure 1. (a) Bright field TEM image of C-TiO_2, and (b) corresponding diffraction pattern.



(a) (b)

Figure 2. (a) EFTEM map of Ti-L_{23}, and (b) corresponding EELS spectra showing C-K and Ti-L_{23} edges.

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