Structural and Magnetic Tailoring of the TiO_2 Nanoparticles via Fe-Incorporation

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Introduction

Nanostructured titania-based materials are considered as promising candidates for energy-related applications such as solar-energy devices and also by virtue of their catalytic potential.[1] Doping these materials with ferromagnetic transition metals such as Fe is anticipated to foster multifunctionality by integrating magnetic, semiconducting and catalytic characteristics. Further, Fe incorporation may improve the catalytic functionality of titania nanostructures due to anticipated modification of the titania band gap. Band gap engineering of titania is critical considering that anatase, the most common crystal structure of titania for photocatalytic applications, has a band gap of 3.2 eV which corresponds to the UV range (10 to 400 nm wavelength), resulting in absorbing only ~4% of the solar spectrum. [2]

In this study, Fe cations are incorporated into titania nanoparticles at a concentration of ~3 at% during a modified sol-gel process.[3] Morphological, structural and magnetic properties of spray-dried pure and Fe-incorporated titania nanoparticles are investigated in their as-made and calcined states (three-hour calcination in air and at 400 °C). Results indicate that Fe incorporation leads to a decrease in the band gap energy and an expansion of the anatase unit cell volume. In addition, an enhanced metallic-like behavior was observed in the calcined Fe-incorporated nanoparticles. Such behavior can be correlated to the electronic density of states that is the number of electrons per unit volume and per unit energy. The observed changes in the band gap, crystal structure and density of states in the Fe-incorporated nanoparticles may be associated with the tailoring of the electronic structure of titania and thus providing insight into the enhancement of the photocatalytic activity of these nanostructures.

Results and Discussion

Scanning electron microscopy indicates that both the spray-dried pure and the Fe-incorporated titania nanoparticles are in the form of 2-10 micron size agglomerates, **Figure 1**. However, the Fe-incorporated agglomerates seem to have a smoother spherical morphology as compared to the pure titania agglomerates, both in the as-made and calcined states.

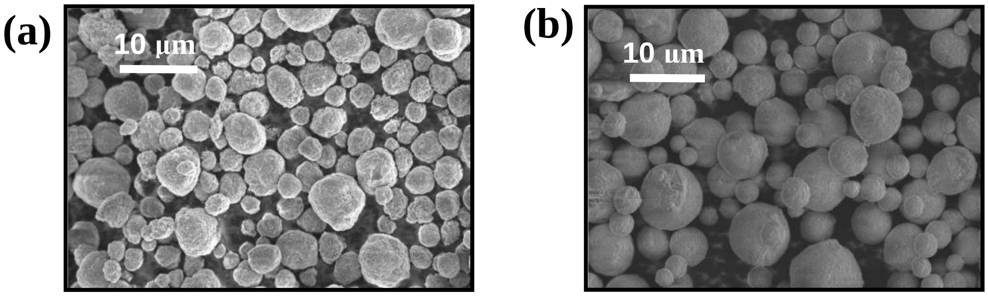

Figure 1. Typical scanning electron micrographs of agglomerations of the as-made (a) pure and (b) Fe-incorporated titania nanoparticles.

UV-Vis spectroscopy shows a decrease in the band gap of Fe-incorporated nanoparticles (2.64 ev ≈ 470 nm) as compared to that of the pure titania nanoparticles (3.19 eV ≈ 390 nm).[3]

Such reduction of the band gap energy by Fe incorporation may make these nanoparticles capable of absorbing a higher fraction of the solar energy by extending their absorbing range from UV to the visible range of the solar spectrum.

X-ray diffraction (XRD) reveals that particles have the anatase structure, both in the as-made and calcined states, along with a minor brookite phase fraction. In addition, Fe-incorporated nanoparticles possess a slightly larger unit cell volume as compared to the calcined pure titania nanoparticles (1.20% ± 0.01% increase). This expansion of the crystal lattice signals incorporation of Fe into the anatase lattice structure.

Connections between the nanoparticles' crystal and electronic structure underlying the nanostructured anatase functionality may be appreciated by analysis of the electronic density of states as revealed by the temperature dependence of the magnetic susceptibility. A direct relation exhibits between the Pauli paramagnetism (χ_{PP}) and the density of states at the Fermi level ($N(E_f)$), through the following equation:

$$N(E_f) = \chi_{PP}/2\mu_B^2, \qquad \text{Eq. (2)}$$

where μ_B is the Bohr magneton. **Figure 2** shows the change in the magnetic susceptibility of the nanoparticles with temperature at 500 Oe. The magnetic data are analyzed by decomposition of the magnetic susceptibility response into temperature-independent Pauli and temperature-dependent Curie-Weiss paramagnetic components. It is noted that calcined Fe-incorporated nanoparticles exhibit an increase in the Pauli paramagnetic signal and thus a higher density of states which can further influence photocatalytic functionality associated with the radiation absorption.[4]

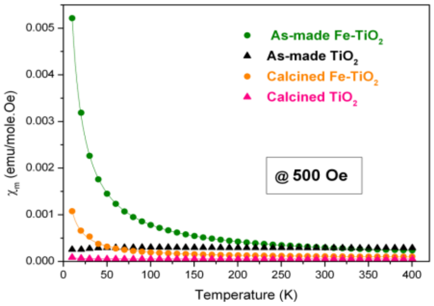

Figure 2. Temperature-dependence of the magnetic susceptibility of the titania-based nanoparticles (superconducting quantum interference device (SQUID) magnetometry).

In summary, the observed changes in the band gap, crystal structure and the density of states in the Fe-incorporated titania nanoparticles may be correlated to the tailoring of the titania band structure, with potential relevance to the photocatalytic capability of these nanostructures.

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