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STUDY OF PROPERTIES OF TITANIUM DIOXIDE NANOPARTICLES.

PhD Thesis

Abstract

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This PhD thesis is based on publications and patent applications (1-9) to which the author contributed considerably. The list of the publications is attached at the end of this text.

Systematic research of the properties of TiO_2 nanoparticles brought new pieces of knowledge into syntheses of titanium dioxide nanoparticles organized in the templated structures. When the structures were used in the solar cells, their solar efficiency significantly surpassed the performance of the conventional TiO_2 films.

The study was focused on the engineering and optimization of parameters of the nanostructures used as anodes in the dye sensitized solar cells (DSC).

Several new technical solutions have been delivered during the work on variety of TiO_2 structures.

First, the factors with an impact on the proper function of the TiO_2 multilayer film were determined

and then, the layer by layer deposition technique was perfected.

Introduction of phosphorus into the templated mesoporous film synthesis protocol represented significant progress. The presence of phosphorus stabilized the TiO_2 surface area at a high temperature and allowed a preparation of a phase pure anatase. The anatase crystal phase purity guaranteed a full coverage of the anatase crystals by the dye. This, together with the large surface area of the structure provided a very high amount of the adsorbed dye on TiO_2. After the improvement of the solar efficiency by approximately 15 % through an increase of the film thickness and modification of the thermal processing, the phosphorus doping brought another 15 % enhancement of the solar efficiency of the solar cells.

Another important step in this work was using this highly productive structure generating electrons in a composite with electrospun fibers. The fibers

radically improved the collection and transport of electrons through the structure.

As a result, two-micron composite films showed similar solar efficiency as many times thicker layers made by the established sol-gel synthesis.

While looking for an optimal concentration of phosphorus in TiO_2 we have succeeded to prepare a monoclinic TiO_2(B) crystal form. The transparent templated TiO_2(B) films consisted of nanoparticles. This crystal form of TiO_2 shows promising electrochemical behavior in the Li-insertion in non aqueous systems. TiO_2(B) may be a suitable replacement for the existing lithium titanate spinel ($Li_4Ti_5O_{12}$) in the lithium batteries. The electrochemical potential of TiO_2(B) vs. lithium and the lithium insertion capacity are very similar to the spinel. The templated TiO_2(B) thin multilayer films were made on the glass substrates covered by a layer of a conductive tin oxide (FTO) on one side. They showed very fast color change during charging and discharging. Switching the colors from transparent to the dark blue during the Li insertion and back took only several seconds. This effect might be used for “Smart Windows”.

Together with the electrochemical properties a specific impact of TiO_2(B) on the shape and crystal structure of the photocatalytically developed silver for $AgNO_3$ solution was studied. The three dimensional dendritic nano crystals of silver typically formed on the nanoanatase films of the same thickness, morphology and specific surface were scarce. The surface of TiO_2(B) film produced several-micrometer-sheets that were only few nanometers thick, and number of one dimensional nano-wires. Otherwise common dendrites of metal silver were practically not present on this type of surface.

There was a remarkable different in the silver growth on the TiO_2(B) synthesized from Cs_2TiO_3,

where the long needle TiO_2(B) crystals propagated along the *b* axis. The silver metal crystals, about 30 nm in size, developed very fast covering the TiO_2(B) whiskers completely. TiO_2(B) crystal growth along the b axis was not observed in the templated films.

Detailed characterization of the structural changes and the description of the sintering processes inside all types of the templated films prepared during this study were provided. A model of sintering explaining these changes was proposed.

Composites consisting of TiO_2 fibers or carbon nanotubes incorporated into the mesoporous TiO_2 nanostructure were also studied. The carbon nanotubes showed an excellent contact with the TiO_2 surface and would be useable as a current collector for instance in the Li battery system.

Discovery of a low-temperature synthesis of titanium oxynitride might be of an importance in the future. When starting with nanofibers the reaction temperature of TiO_2 with ammonia can be as low as 500°C. Materials forming in the reaction have cubic structures and are highly electrically conductive. The nanofibrous morphology stays intact and the particle size of TiO_xN_y with the nitrogen content over 30 atomic percent is similar to the particle size of the anatase, from which they had formed.

Rutile reaction with ammonia was very specific. Although it was obvious that the transformation occurs, it was impossible to detect the reaction progress with XRD.

Another fact deserving an attention was that the transformation of nanoanatase into TiO_xN_y is fully reversible. Nanoanatase forms even at temperatures as high as 800°C, while the original starting (uncycled) material recrystallizes into rutile.

When TiO_xN_y is fired in an oxygen atmosphere at otherwise similar conditions (600°C), total destruction of the nanofibrous structure, intensive fusion and a crystal structure change occur. TiO_xN_y is immediately converted into relatively large crystals of rutile and the color of the material turns from black to white instantly.

Because of the expected practical use of the synthesis a patent application was filed.