

## POLYMORPHIC TRANSFORMATION OF TITANIUM DIOXIDE CAUSED BY HEAT TREATMENT OF PROTONIC LEPIDOCROCITE TITANATE

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### ABSTRACT

The polymorphic phases of titanium dioxide were successfully prepared by heat treatments of protonic lepidocrocite titanate,  $H_{0.54}Ti_{1.865}\square_{0.135}O_4 \cdot 0.5H_2O$  at various temperatures. The prepared powders were characterized with EDX (Energy Dispersive X-ray), Scanning Electron Microscopy (SEM), X-rays Diffractometer (XRD), Raman Spectroscopy, and High Resolution Transmission Electron Microscopy (HRTEM). The effect of calcination temperature on the phase structure and morphology of the heated samples was investigated. The research indicated that the protonic titanate,  $H_{0.54}Ti_{1.865}\square_{0.135}O_4 \cdot 0.5H_2O$  ( $\square$  = vacancy), lost the interlayer water by being heated up to 200 °C to produce a dehydrated phase,  $H_{0.54}Ti_{1.865}\square_{0.135}O_4$ . Above 300 °C, the dehydrated phase,  $H_{0.54}Ti_{1.865}\square_{0.135}O_4$ , completely transformed to  $TiO_2(B)$  and anatase was obtained as pure phase at 600 °C. The phase transformed as the following process:  $H_{0.54}Ti_{1.865}\square_{0.135}O_4 \cdot 0.5H_2O \rightarrow H_{0.54}Ti_{1.865}\square_{0.135}O_4 \cdot 0.25H_2 \rightarrow H_{0.54}Ti_{1.865}\square_{0.135}O_4 \rightarrow TiO_2(B) \rightarrow TiO_2$ -anatase.

**Keywords:** layered compound, titanium dioxide, lepidocrocite, phase transformation, heat treatment

### INTRODUCTION

Titanium dioxide ( $TiO_2$ ) is considered to be one of the most promising materials due to its excellent physicochemical stability, high oxidation affinity, mechanical hardness, superior photo-reactivity and novel optoelectronic properties. It is widely used as white pigment in paints, cosmetics, photoelectrochemistry and catalyst carrier in industry [1]. Titanium dioxide as an n-type semiconductor with a wide energy band gap is well-known for its potential applications in the field of photovoltaic devices [2-6], superhydrophilic and light-induced amphiphilic surfaces [7-10] and antibacterial applications [11-13]. It can be also applied in heterogenous photocatalysis [14]. The photocatalytic activity of  $TiO_2$  is markedly influenced by the microstructure, polymorphic phases, particle shape, crystallite size, crystallinity, and specific surface area.  $TiO_2$  nanoparticles show high photocatalytic activities because they have a large surface area per unit mass and volume, and hence facilitate the diffusion of excited electrons and holes towards the surface before their recombination. This process involves a large variety of reactions, for example, partial or total oxidation, dehydrogenation, hydrogen transfer, metal deposition, water detoxification, or gaseous pollutant removal [15-19].

Titanium dioxide has eleven polymorphic phases: anatase (tetragonal,  $I_4/amd$ ) [20], rutile (tetragonal,  $P4_2/mnm$ ) [21-22], brookite (orthorhombic,  $Pbca$ ) [23],

$TiO_2(B)$  (monoclinic,  $C2/m$ ) [24],  $TiO_2(H)$ -hollandite (tetragonal,  $I4/m$ ) [25],  $TiO_2(R)$ -ramsdellite (orthorhombic,  $Pbnm$ ) [26],  $TiO_2$ -columbite type  $\alpha$ - $PbO_2$  ( $TiO_2-II$ ) (orthorhombic,  $Pbnm$ ) [27-28],  $TiO_2$  baddeleyite type ( $TiO_2-MI$ ) (monoclinic,  $P2_1/c$ ) [29-30],  $TiO_2$ -orthorhombic ( $TiO_2-OI$ ) (orthorhombic,  $Pbca$ ) [31],  $TiO_2$  fluorite type  $CaF_2$  (cubic,  $Fm3m$ ) [32] dan  $TiO_2$  cotunnite type (orthorhombic,  $Pnma$ ) [33]. Rutile is a stable phase, while anatase and brookite are metastable and will be transformed into a thermodynamically most stable rutile phase at higher temperature after thermal treatment. The low temperature anatase phase is irreversibly transformed to rutile phase on heat treatment above 450 °C. The transformation from anatase to rutile is metastable-to-stable transformation and there is no equilibrium temperature of the transformation. The transformation temperature range varies from 400 °C to 1200 °C, depending on the grain size, presence of impurities, dopants, precursor material and synthesis method [34].

The photocatalytic performance of  $TiO_2$  can be optimized by microstructural and macrostructural control on the morphology of the material because of the intimately morphology-dependent characteristic of the photocatalytic properties. It is interesting and necessary to investigate the process of the  $TiO_2$  phase transformation, both from a scientific and from a technological point of view. Nanostructured  $TiO_2$  materials can be prepared by dry and wet processes. In this work, the  $TiO_2$  polymorphic phases are prepared

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