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Direct synthesis of TiO_2 nanoparticles by using the solid-state precursor TiH_2 powder in a thermal plasma reactor

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ABSTRACT

We attempt the direct synthesis of TiO_2 by using the solid state precursor TiH_2 powder with oxygen in a thermal plasma reactor. Nanocrystalline titanium dioxide powder has been synthesized by using thermal plasma synthesis in a non-transferred arc thermal plasma reactor. The thermal plasma-synthesized powder product consists of nano-sized particles of anatase and rutile phases of titanium dioxide. Particle compositions were observed on collecting powder from different positions of the reactor and varying the amount of flow rate of reactive gases (O_2). The characteristics of the powder such as particle size, size distribution and phases were analyzed using various techniques such as XRD, SEM, TEM, XPS, EDS and particle size analyzer. UV–visible reflection spectroscopy of the plasma-synthesized TiO_2 powders showed the absorbance in the visible region leading to effective photocatalytic activity, which is clearly confirmed from the XPS analysis. XPS analysis reveals the presence of –OH bonds on the surface of nanoparticles, which is the significant evidence of better quality of powders in comparison to other methods. Also, we have investigated the phase transformation phenomenon of anatase to rutile. At 1000 °C, complete transformation of the anatase to rutile occurs. Powders prepared in this procedure are white in colour and their diameter varies from 10 nm to 150 nm. Average particle size distributes in the range of 20–50 nm. The unique property about the plasma-synthesized powders is high resistance to heat treatment, with enhanced photocatalytic activity.

Keywords: Titanium hydride; Thermal plasma; Phase transformation; Titanium dioxide

1. Introduction

Apart from use in paint industries, titanium oxide is being extensively used to address a variety of environmental pollution problems. Titania based photocatalysts are used for a variety of applications such as decomposition of unwanted and toxic organic compounds and destruction of pollutants from contaminated water, air and harmful bacteria (Oh and Park, 2001). Research is going on the synthesis and processing of nano-crystalline materials because of their wide range of applications for improving material structures and functional properties. The high efficiency of the photocatalysis of TiO_2 nano-crystalline, in combination with their structural and thermal stability makes this material well suited for cleaning air, water, soil and for degrading hazardous chemicals (Sandim et al., 2005). Titanium dioxide based catalysts offer certain specific advantages. The band gap of TiO_2 is about 3.2 eV and can be shifted to the visible region by suitable doping (Li and Ishigaki, 2004). Titanium oxide is non-toxic in nature, photo-chemically stable and relatively inexpensive. In near future, depending on the particle morphology, crystal structure, size distribution and phase compositions, titanium oxide will find more versatile applications. TiO_2 is a polymorphic material that exits in three crystalline polymorphs, namely, stable rutile (tetragonal), metastable anatase (tetragonal) and metastable brookite (orthorhombic). Anatase and rutile are

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common polymorphs of synthetic TiO_2, while brookite is a high-pressure phase (Oh and Park, 1998) and is occasionally observed as a by-product along with either anatase or rutile. The anatase phase transforms into rutile over a wide range of temperatures.

Titanium dioxide powders are commonly produced by two processes such as sulfate and chloride processes. Chloride process is much cleaner process when compared to sulfate process and safer also. Recent preparation techniques tend towards sol–gel, flame synthesis and thermal plasma methods. The main disadvantages of sol–gel lie in the use of large amount of energy, particle growth and aggregate formation resulting from crystallization of as-made amorphous or low-crystalline powders (Bora et al., 2010). Flame synthesis is relatively inexpensive and simple although phase control of the product is problematic.

A new method of direct synthesis of solid-state precursor using titanium hydride has been developed for the production of titanium dioxide nanoparticles in thermal plasma jet. The uniqueness about this process is that particle size reduces remarkably when compared to other processes with enhancement in photocatalytic activity. Although earlier researchers already have done some work on this related area, this process shows direct synthesis of solid-state precursor TiH_2, which results in the production of nanoparticles having high resistance to heat treatment. Thermal plasma synthesis is known as a clean process. Thermal plasma synthesis is a unique technique that takes the advantage of high temperature and high enthalpy of the thermal plasma jet. It is a versatile process, having short processing time, large throughput and a one step process to obtain the nanopowders. In present investigation a process has been developed for preparation of crystalline ultra-fine TiO_2 powders. Nano-powders were characterized using X-ray diffractometer (XRD), scanning electron microscope (SEM), UV–visible spectrometer, particle size analyzer (PSA) and transmission electron microscope (TEM).

2. Thermodynamic calculations

The chemical equilibrium compositions in various systems were calculated using a software program based on Gibb's free energy minimization. The results are useful in the preliminary experiment. Fig. 1(a) represents phase equilibrium of titanium hydride in argon atmosphere as a function of temperature. The sample is inactive and remains same in argon atmosphere. Plasma gases are also taken into account in these thermodynamic calculations, but are not shown in the plots due to their higher content. The graph shows that at temperature above 4800 K, which is found inside plasma jet, only the mono atomic H and Ti are stable. In the temperature range of 2300–3300 K, the mono atomic gases become unstable and recombine to form new species. The possible reactions that may take place in this zone during the reaction process are as follows

$$\mathrm{Ti\,(g)} \rightarrow \mathrm{Ti\,(l)}, \quad \mathrm{2H\,(g)} \rightarrow \mathrm{H_2\,(g)}$$

In the temperature range of 1300–2300 K, Ti in the form of liquid becomes unstable and the reaction is as follows

$$\mathrm{2Ti\,(l)} \rightarrow \mathrm{Ti\,(s1)} + \mathrm{Ti\,(s2)}$$

At temperature below 800 K, Ti and H recombine to form solid TiH_2

$$\mathrm{Ti\,(s)} + \mathrm{H_2\,(g)} \rightarrow \mathrm{TiH_2\,(s)}$$

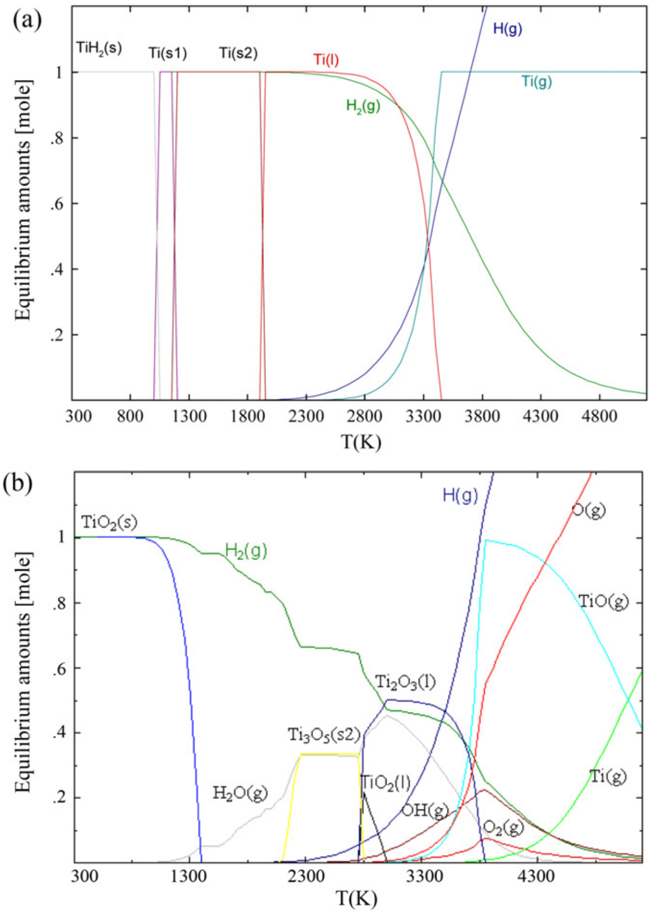

Fig. 1 – (a) Chemical equilibrium composition of TiH_2 with argon atmosphere. (b) Chemical equilibrium composition of $TiH_2 + O_2$ in argon atmosphere.

However, in the presence of oxygen between 300 and 1800 K, TiO_2(s) is formed after reaction with oxygen gases as shown in Fig. 1(b). Plot shows that at temperature above 4800 K, which is found inside plasma jet, only the mono atomic gases H, Ti and O are stable. The possible sequential reactions are as follows:

(i) $\mathrm{Ti\,(g)} + \mathrm{O\,(g)} \rightarrow \mathrm{TiO\,(g)}$ at the temperature range of 3800–4300 K

(ii) (a) $\mathrm{2TiO\,(g)} + \mathrm{O\,(g)} \rightarrow \mathrm{Ti_2O_3\,(l)}$ (b) $\mathrm{O\,(g)} + \mathrm{H\,(g)} \rightarrow \mathrm{OH\,(g)}$ 2300–2800 K

(iii) $\mathrm{(3/2)Ti_2O_3\ (l)} + \mathrm{(1/2)OH\ (g)} \rightarrow \mathrm{Ti_3O_5\ (s)} + \mathrm{(1/4)H_2\ (g)}$ 2300–2800 K

(iv) $\mathrm{(1/3)Ti_3O_5\ (s)} + \mathrm{(2/3)H_2\ (g)} + \mathrm{O\ (g)} \rightarrow \mathrm{TiO_2\ (s)} + \mathrm{(2/3)H_2O\ (l)}$ below 1300 K

TiO_2 and water vapor H_2O (g) remain stable at room temperature. TiO_2 can be collected in the form of nanopowder from the reactor.

Free energy minimization plots for chemical equilibrium were calculated to predict the thermodynamic behavior of the Ti–H system under different operating conditions. The results of this investigation showed a significant production of titanium dioxide in the presence of reactive gas oxygen in suitable temperature zone. This prediction draws an overall view of the theoretical feasibility of the experiments. The calculated result shown in Fig. 1 gives a brief idea about the process parameters to be planned for experimental analysis.