Materials Letters 219 (2018) 72–75

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Featured Letter

Shock wave induced anatase to rutile TiO_2 phase transition using pressure driven shock tube

S. Kalaiarasi, A. Sivakumar, S.A. Martin Britto Dhas, M. Jose *

Department of Physics, Sacred Heart College (Autonomous), Tirupattur-635601, India

ARTICLE INFO

Article history:
Received 11 November 2017
Received in revised form 24 January 2018
Accepted 14 February 2018
Available online 14 February 2018

Keywords:
Nanoparticles
Phase-transformation
FT-Raman
X-ray techniques
Crystal structure

ABSTRACT

Pressure driven shock tube was employed to switch TiO_2 nanoparticles from anatase to rutile phase at an applied pressure of about 2.683 MPa. The crystal structure and surface morphology of the anatase-rutile phase transformation are investigated for pre and post loaded shock using X-ray diffraction, FT – Raman spectroscopy and transmission electron microscopy respectively. The results from the experimental investigations elucidated that the TiO_2 nanoparticles under post shock facilitated the formation of new crystallographic phase (rutile) from anatase phase.

1. Introduction

Interest in titanium dioxide has received tremendous interest among research community and industrialists in energy and environmental catalysis owing to its fascinating properties at nano dimensions [1]. Most importantly, TiO_2 has found its utility in photocatalyst, chemical sensor, dielectric materials for capacitors, filters, ceramics, cosmetics and fiber manufacturing, etc [2]. Reports available in the literatures indicate that, interaction of materials with shock heated gas leads to formation of a new solid or stabilization of a material in new crystallographic phase. Phase transformation can be induced in materials under extreme pressure and temperature due to application of shock waves for a very short duration of time [3]. Phase transformation of Titanium dioxide nanoparticles (TiO_2 NPs) using shock waves with different shock wave loading techniques were employed to modify its structure. Interesting crystallographic phase transformation from anatase TiO_2 to N doped rutile TiO_2 was demonstrated using shock compressed nitrogen gas at high temperature for short duration of 3.5 ms [4]. TiO_2 NPs is found to transform from tetragonal rutile to the monoclinic baddeleyite structure between 20 and 30 GPa [5]. The morphology-tuned structural phase transition from anatase to baddeleyite phase under high pressure was found in the anatase TiO_2 structure [6–7].

In this paper, we have demonstrated the impact of shock waves on the morphology and structural changes from anatase to rutile phase transition of TiO_2 NPs. The pressure induced phase transitions in TiO_2 NPs is studied using powder XRD analysis and FT – Raman Spectroscopy and the corresponding morphological evolution is studied using transmission electron microscopy (TEM) analysis. The findings suggest that the anatase phase of TiO_2 was stable upto 60 shocks of Mach number 2.7. Further, the stability of anatase phase below 90 shocks at applied pressure (2.367 Mpa) and temperature (987 K) was demonstrated. However, when the number of shocks reaches 90, the anatase TiO_2 undergoes shock induced phase transitions to rutile which could be due to the lattice dynamical instabilities caused by the applied shock.

2. Synthetic procedure for material preparation

Typical procedure was adopted to prepare the TiO_2 NPs [8]. Aqueous titanium citratocomplex solution was prepared by dissolving titanium isopropoxide in anhydrous citric acid solution at 1 mol concentration and the mixture was stirred for 30 min. Then 25 wt% aqueous Hexamethylenetetramine and ammonium was added drop wise to adjust the pH at 6.0 and the above solution was transferred into teflon lined autoclave maintained at 200 °C for 12 h in an electric hot air oven. The product was decanted with ethanol and thereafter the resultant product was calcinated at 600 °C for further analyses.

3. Experimental description

Indigenously designed semi automated table top pressure driven shock tube (PDST) capable of producing shock waves of about

* Corresponding author.
E-mail address: jose@shctpt.edu (M. Jose).

https://doi.org/10.1016/j.matlet.2018.02.064
0167-577X/

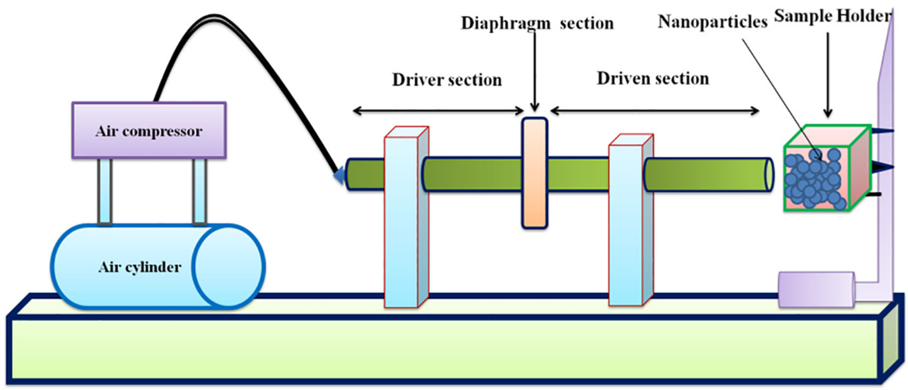

Fig. 1. Schematic diagram of pressure driven shock tube.

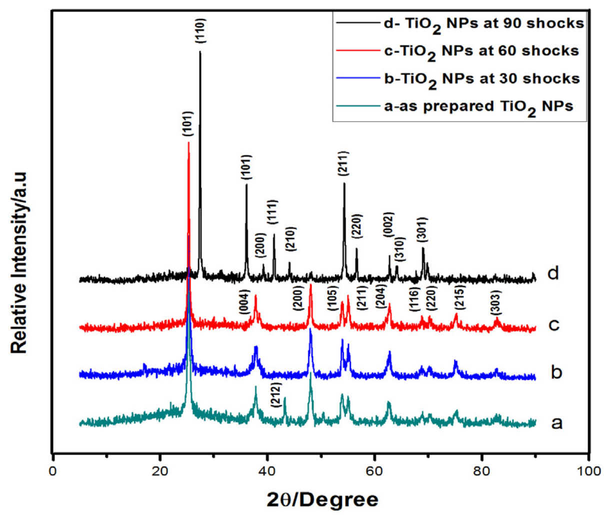

Fig. 2. X-Ray diffraction intensities of TiO_2 NPs.

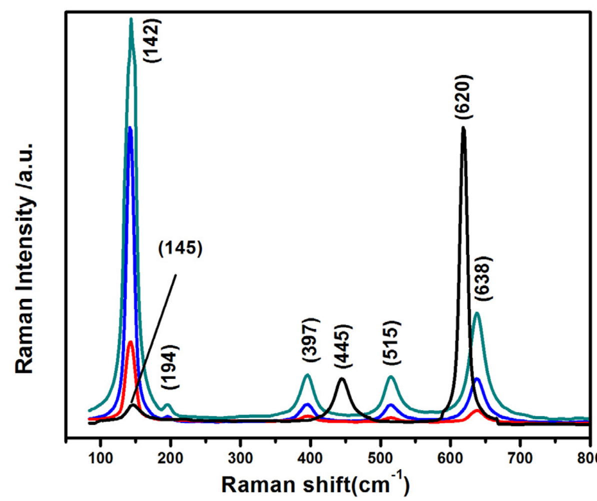

Fig. 3. Raman spectra of TiO_2 NPs.

1–5 Mac numbers is shown in Fig. 1. Input pressure unit is employed to raise the pressure in driver section and at a critical pressure, the diaphragm raptures, consequently, shock wave propagates into the driven section and tends to impact the freshly prepared TiO_2 NPs which is placed 1 cm apart from the open end of the driven section. For this investigation, the sample is loaded with number of shock waves viz,. 30, 60 and 90 with Mach number 2.7 at applied dynamic pressure (2.367 MPa) and temperature (987 K) and the influence of shock waves on the structural and morphology changes of the TiO_2 nanoparticles was systematically analyzed.

4. Result and discussion

4.1. Powder XRD analysis and Raman spectroscopy analysis

Investigations of XRD analysis (Fig. 2a) indicates that as synthesized TiO_2 NPs comprises of mixed phase with a characteristic anatase phase at $2\theta = 25.12^{\circ}(101)$, $37.9^{\circ}(004)$, $47.6^{\circ}(200)$, $53.4^{\circ}(105)$, $54.08^{\circ}(211)$, $62.8^{\circ}(204)$, $68.7^{\circ}(116)$, $70.3^{\circ}(220)$,$75.05^{\circ}(215)$ and $82.3^{\circ}(303)$ and a reflection of brookite peak at $2\theta = 43.22^{\circ}(212)$ (JCPDS No. 86-1157, space group = $I4_1$/amd, lattice parameter, a, b = 3.7913(3) and c = 9.527(2) Å). XRD patterns obtained for the sample with shock number at 30 and 60 do not show any additional peaks, however, complete relapse of the brookite peak takes place (Fig. 2b and c). Less impact over reduction in interlayer spacing and the collapse of the atomic particles endures the formation of phase pure anatase TiO_2 NPs and anatase phase remains stable upto 60 numbers of shocks. Interestingly, when the number of shocks is increased to 90, anatase phase disappears completely and rutile phase is evolved which is evident by the appearance of diffraction peaks (Fig. 2d) corresponding to the planes (110), (101), (200), (111), (210), (211), (220), (002), (310) and (301) (JCPDS No.87-0920, space group: $P4_2$/mnm, lattice parameter a, b = 4.591(3) Å, and c = 2. 959(2) Å). The sharp and intense peaks suggest that transformed rutile TiO_2 is highly crystalline. The calculated grain size of as prepared TiO_2 NPs is 21 nm and shock induced anatase phase TiO_2 NPs using Scherrer equation at shock 30, 60, 90, is 18 nm, 31 nm and 44 nm respectively, which clearly elucidates the impact of shock in phase transformation.

The shocks induce the grain growth of the particle, as demonstrated by TEM and crystallite sizes analyses from Scherrer equation. Thus, when it reaches the critical particle size, from the thermodynamic point of view, anatase transforms to rutile. This happens because the phase stability in nanoscale is directly related to the grain sizes of the particles. Fig. 3(a–d) shows the Raman spectra of as prepared and post shock loaded TiO_2 NPs. Initially, the as synthesized TiO_2 NPs contains mixed phase as evidenced from the appearance of four Raman modes at 142 cm^{-1}, 397 cm^{-1}, 515 cm^{-1}, 638 cm^{-1} corresponding to anatase phase and one peak corresponding to brookite phase at 194 cm^{-1} (Fig. 3a) The high intensity peak at 142 cm^{-1} is in good agreement with the Raman spectrum of polycrystalline anatase TiO_2 which is due to the linear combination of asymmetric bending of O—Ti—O bonds