Journal of Alloys and Compounds 676 (2016) 591–600

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Strain induced phase formation, microstructural evolution and bandgap narrowing in strained TiO_2 nanocrystals grown by ball milling

Gone Rajender [a], P.K. Giri [a, b, *]

[a] Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India
[b] Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati 781039, India

ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form
16 March 2016
Accepted 21 March 2016
Available online 22 March 2016

Keywords:
TiO_2 nanocrystals
Strain
Williamson-Hall plot
Phase formation
Band gap engineering

ABSTRACT

Band gap narrowing in metal oxide semiconductor nanostructures is important and advantageous for various potential applications including visible light photocatalysis. We present a systematic study on the anomalous strain evolution, phase change and band gap narrowing in TiO_2 nanocrystals (NCs) as a result of ball milling. In addition to the size reduction and strain evolution with milling time, we report the formation of a new phase of TiO_2 with milling, as identified in the XRD pattern and Raman spectra for the first time. Besides the tetragonal anatase phase of TiO_2 NCs, two additional peaks centered at $2\theta = 31.28^\circ$ and 41.60° evolve with milling, and it corresponds to the $(\bar{1}\ 12)$ and (312) planes of Ti_3O_5, respectively. Further, our results show that the band gap of TiO_2 NCs reduces with increasing strain and lowest band gap achieved in strained TiO_2 is 2.71 eV, consistent with a recent theoretical calculation. The evolution of the crystallite size, strain, stress and energy density was evaluated from the line shape analysis of the XRD pattern using various models, such as uniform deformation model, uniform stress deformation model, uniform deformation energy density model and the results are compared with those obtained directly from HRTEM analyses. The increased d-spacing with milling time was attributed to the tensile strain in TiO_2 NCs. Direct evidence of lattice strain and strain relaxation is provided from HRTEM imaging and differential scanning calorimetry analyses. Our results demonstrate strain engineering of TiO_2 to achieve narrow bandgap in anatase TiO_2 NCs, which are promising for visible light photocatalytic and other emerging applications.

1. Introduction

Titanium oxide (TiO_2), an important wide band gap semiconductor, has been studied extensively in the past decades due to wide range of applications in photo catalysis, solar cells, fuel cells, chemical sensors, biomedical, lithium storage, glass coating, self-cleaning etc. [1–10] It is well known that the particle size and crystal morphology play an important role in photocatalytic, thermal and magnetic properties of TiO_2 [11–13]. The functional properties of TiO_2 are strongly dependent on its phase and microstructure [14–18]. Indeed, the crystallite size is critical for phase stability, and the presence of micro- and/or macro-strains may affect the photoinduced hydrophilicity [19]. The phase change of TiO_2 based compounds (Ti_3O_5, Ti_2O_3, Ti_4O_7) etc. plays an important role for various applications, like heat storage, sensors [20]. Among these polymorphs, Ti_3O_5 is one of the most promising material for optical memory applications [21]. Many synthesis techniques have established for controlled synthesis of TiO_2 nanocrystals (NCs), such as hydrothermal [22], sol-gel [14], sonochemical and microwave [16], microemulsion-mediated hydrothermal [18], wet chemical [23] methods etc. Among these techniques, ball milling is a simple and low cost technique without involving any complex chemical synthesis.

Several groups reported the evolution of strain with size reduction in NCs of different semiconductors, such as Si NCs [24], Ge NCs [25] and ZnO NCs etc. [26–28] However, only a few reports investigated on the role of strain and size induced broadening of XRD peaks in TiO_2 NCs [29]. Recently, Ansari et al. reported the gold and silver plasmonic nanoparticles mediated band gap engineering

* Corresponding author. Department of Physics, Indian Institute of Technology Guwahati, Guwahati 781039, India.
E-mail address: giri@iitg.ernet.in (P.K. Giri).

http://dx.doi.org/10.1016/j.jallcom.2016.03.154
0925-8388/

in TiO_2 [30,31]. Tripathi et al. reported the temperature dependent variation of strain in TiO_2 NCs [32]. The strain analysis has been mostly limited to Williamson-Hall (W–H) method. However, an extensive analysis of the X-ray diffraction (XRD) data by means of fitting of line shape with various models has not been reported earlier. Besides the size and strain, the band gap plays the leading role to tune the optoelectronic properties. Bulk TiO_2 band gap falls in the UV region, thus it limits the use in optoelectronic and visible light photocatalysis. Unfortunately, no experimental report is available on the band gap modification of TiO_2 NCs by strain engineering, while only theoretical report [33] is available on band gap reduction using strain. Denis et al. [34] reported that strain is created in bulk TiO_2 surface by Ar ion bombardment, but its influence on the band gap evolution was not studied. Here, we demonstrate the band gap tuning by strain engineering with a simple ball milling approach. This is very useful for photocatalytic and optoelectronics applications of TiO_2. To the best of our knowledge, no experimental report is available on band gap modification of TiO_2 using simple ball milling technique. The anomalous strain behaviour reported here has not been addressed earlier in the literature.

Generally, for the small NCs the XRD pattern is different from its bulk crystalline counterpart. The deviation from perfect crystalline order leads to a broadening of the diffraction peaks. It is known that the mechanical alloying may induce a large amount of strain in the powders [35]. XRD line profile analysis is a simple and powerful tool to estimate the crystalline size and lattice strain [36]. Out of different available methods to estimate the crystallite size and lattice strain, the W-H analysis, pseudoVoigt function, Rietveld refinement, and Warren Averbach analysis are mostly common [37–39]. W-H analysis is a simplified integral breadth method where both size-induced and strain-induced broadenings are investigated by considering the peak width as a function of 2θ [27]. To the best of our knowledge, band gap modification by strain and modified W-H method has not been discussed extensively for the calculation of size and strain in TiO_2 NCs.

In the present work, we have grown TiO_2 NCs of sizes down to 11 nm by simple ball milling method. As a result of milling, a new phase of TiO_2 is reported for the first time. The particle size and strain are calculated in a systematic way by means of XRD analysis and direct imaging i.e. by transmission electron microscopy (TEM). Different models are utilized to calculate crystallite size and strain from XRD line profile and the correlation between the different models are made for different parameters. The band gap modification achieved with the combined effect of strain and oxygen vacancy defects in TiO_2 NCs has been explored in detail. In addition to the XRD, the phase change and nature of strain are further confirmed from the Raman spectroscopy. Finally, the strain relaxation and structural changes are further investigated by DSC measurements.

2. Experimental details

TiO_2 NCs are prepared from commercially available TiO_2 powder with initial average particle size ~80 nm (>99% purity) using mechanical ball milling method. Ball-milling was performed at 350 rpm for the duration up to 40 h in a ZrO_2 vial (Restch, PM100) under ambient condition. Small ZrO_2 balls (diameter 5 mm) were used for the ball-milling and this ensured contamination-free milling process. The ball to powder weight ratio was taken as 10:1. The milled samples were collected at 4, 8, 12, 16, 20, 30 and 40 h duration. Very fine TiO_2 NCs with few nanometer sizes were obtained after milling. For the convenience of subsequent discussion, we denoted the unmilled, 4 h, 8 h, 12 h, 16 h, 20 h, 30 h and 40 h milled TiO_2 NCs samples as T0h, T4 h, T8 h, T12 h, T16 h, T20 h, T30 h, and T40 h, respectively. Post growth annealing experiment was conducted at 350 °C for 90 min using a quartz tube mounted inside a muffle furnace, in air atmosphere. Note that the 16 h milled annealed sample is named as T16 hA.

3. Characterizations

XRD pattern is obtained with Rigaku RINT 2500 TTRAX-III using Cu K_α radiation at the operating voltage 50 kV and current 180 mA. For careful determination of average nanocrystals size, internal lattice strain, and, energy density, XRD data was collected at a slow scan rate of 0.002° per second. For the diffraction peak of (101) planes, all the samples were scanned in the range 23–27 (2θ) with a very slow scan rate of 0.0005° per second. Particle size analysis, high magnification surface morphologies, crystallinity and lattice spacing of the samples were studied with transmission electron microscopy (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED) patterns (JEOL-JEM 2010 operated at 200 kV). Specimens for HRTEM investigations were prepared by dispersing powder particles in ethanol and drop casting them onto the Cu grid of 400 meshes (Pacific Grid, USA). Raman analysis of the samples was performed in Raman spectrometer (Horiba, LabRam HR) with excitation wavelength 514.5 nm. In order to avoid the laser heating induced Raman shift, we have performed the Raman measurements at very low laser power (0.9 mW). The UV-visible diffuse reflectance spectroscopy (DRS) measurements were performed using a commercial spectrophotometer equipped with integrating sphere (PerkinEmler, UV win Lab). To study the strain relaxation and structural changes, the DSC/TGA measurements were performed in STA 449 F3 Jupiter DSC analyser (Netzsch, Germany) with high temperature tungsten furnace (1700 °C) with heating rate of 5 °C/min by purging the high purity Ar gas. Details of the photoluminescence and photocatalysis experiment are provided in the Supporting information, SI-1.

4. Results and discussion

4.1. XRD analysis

Fig. 1(a) shows the comparison of the XRD pattern of different TiO_2 NCs grown by ball milling along with the unmilled TiO_2 powder, while Fig. 1(b) shows a magnified view of the comparison of XRD pattern of all the samples in range ($2\theta = 24–26°$). Inset of Fig. 1(b) represents the shift in XRD peak for T16 h sample before and after annealing. The plotted curves are vertically shifted for clarity. All the peaks labelled in Fig. 1(a) correspond to the anatase phase of TiO_2. Two new peaks appear after 4hr milling and become prominent for the higher milling time (indicated by "*" in Fig 1(a)). Note that, these peaks were not seen in case of unmilled sample. For the size and strain calculations, all XRD peaks were fitted with Gaussian line shape to determine the precise peak position and full width at half maximum (FWHM) of the peaks. From the fitted parameters, it was observed that the FWHM of the peaks gradually increases with increasing milling time. This broadening confirmed the size reduction and the development of strain in the TiO_2 NCs [26,40]. In addition to the peak broadening, we also observed a shift in the peak position. The peak shift after milling might be due to different kinds of strain (tensile and compressive) developed in the TiO_2 NCs. The fitted parameters (peak centre and FWHM) of (101) peak of all the samples are shown in Table 1. It is clear that the peak centres are shifted towards lower 2θ values with increasing milling time up to 16 h and it indicates the presence of the tensile strain in the NCs. Note that the T16 h sample shows the highest peak shift as compared to the other samples. With further increase of milling time, the peak centres are shifted towards higher 2θ value as