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Anharmonicity induced faster decay of hot phonons in rutile TiO₂ nanorods: a Raman spectromicroscopy study†

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Temperature-dependent Raman spectromicroscopy of rutile TiO₂ nanorods has been studied here to understand the effect of thermal perturbations on different Raman-active phonon modes. The TiO₂ nanorods, characterized using electron microscopy, X-ray diffraction and Raman spectroscopy, were prepared using a hydrothermal method. Raman spectra, recorded at temperatures higher than room temperature, have been analyzed within the theoretical framework developed by considering the anharmonicity of hot phonons. Different temperature-dependent responses were observed for E_g and A_{1g} modes with the latter being immune with respect to the Raman peak position. The experimental results indicated a dominant role of phonon–phonon kinematics on peak shifts and broadenings in the E_g Raman mode, confirming the prevalence of the anharmonic effect. The temperature-dependent red-shift in the peak position and broadening of the Raman E_g mode have been explained using three or four phonon decay processes. A consolidated insight, by showing a good agreement between experimental and theoretical frameworks, about the behavior of phonons under the influence of elevated temperatures has been presented.

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Introduction

Transition metal oxides and their nanoparticles have received immense attention from scientists and industry due to their extraordinary applications in the modern technological world.^{1–3} Among these, titanium oxide (TiO₂) has been considered as a “functional building block”, which can be appreciated from the quanta in which this material is manufactured (millions of tons) for various applications as pigment, paint additive, and sunscreen, to name a few simplest uses leaving the sophisticated applications in optoelectronics, catalysis, biomedical, energy and environmental applications.^{4–9} Nanostructures of TiO₂^{10–14} have attracted exclusive interest due to

their chemical stability and low toxicity.^{15,16} Under ambient conditions, TiO₂ is known to exist in eight crystalline polymorphs,¹⁷ of which only three, namely rutile (tetragonal),¹⁸ anatase (tetragonal)¹⁹ and brookite (orthorhombic) phases occur naturally.^{20,21} Though each of these polymorphs exhibit distinct properties, the rutile phase is the thermodynamically preferred²² form at all temperatures. Similar to its bulk form, nanostructured rutile TiO₂ is also important because it exhibits advantageous properties^{23–25} compared to anatase including higher absorption in the visible light, and better chemical stability,^{26–28} making it suitable for numerous applications.^{29–31} Looking at its technological importance, basic properties of this phase has also been explored.³² However, the understanding of anharmonic effects that prevails at temperatures higher than room temperature is quite special about the behavior of these hot phonons, and thus needs further investigation.

Raman spectroscopy^{33–37} is one of the best non-destructive techniques to understand microscopic properties and the best one to investigate the behavior of phonons. Advanced techniques, such as Raman microscopy and thermal mapping, have added new capabilities to the Raman spectroscopy as a tool for investigating and understanding various aspects of (nano-) materials.^{38–44} Raman spectroscopy can identify different Raman active vibration modes, namely B_{1g}, E_g, A_{1g} and B_{2g}, and any change in their vibrational energies and the corresponding phonon spectrum at elevated temperatures.^{38,45–47}

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Temperature-dependent (TD) Raman spectroscopy,^{48,49} due to its fundamental importance in calculating various parameters such as coefficient of thermal expansion, and phonon-lifetime, can be used to investigate the presence of any anharmonicity as well. Since the phonon frequency and lifetime experimentally manifest themselves in terms of Raman peak position and Raman width, any changes in these Raman parameters can be used to understand and quantify the perturbation that affects the underlying physical property. The TD peak shift of a Raman phonon mode provides valuable information on the effect of thermal perturbation on phonon scattering processes and causes Raman peak broadening due to reduced lifetime with thermal expansion of the crystal lattice. Raman study on anatase TiO₂ nanorods (TNRs) has been carried out to a great extent,^{50–52} whereas that of rutile phase has been carried out only by a few research groups,^{40,53,54} and carrying out more studies is required to present a holistic picture about the different aspects related to anharmonicity in low dimensional TiO₂.

The aim of the present study is to investigate anharmonic effects on phonons present in rutile TNRs when temperature is raised above room temperature. Rutile TNRs have been prepared *via* a hydrothermal method on a fluorine-doped tin oxide (FTO) substrate and TD Raman spectra were recorded in the temperature range of 300–725 K have been analyzed. The experimentally obtained TD Raman data have been discussed within the theoretical framework developed by Balkanski *et al.*⁴⁹ to understand how the anharmonic effects manifest in terms of phonon mode energy and their lifetimes. A good correlation between the experimental observations and theoretical model was obtained when a three-phonon decay was considered for the E_g mode, whereas the A_{1g} mode was found to be immune to the thermal perturbations. The present approach is free of complex calculations and independent of numerous variables unlike some other methods, such as molecular dynamic simulation, which is quite complex and requires a lot of mathematics. Moreover, the present study has been done for higher temperatures (higher than room temperature) by taking the reference at room temperature.

Experimental details

Rutile TiO₂ nanorod arrays were prepared on fluorine-doped tin oxide (FTO) substrates (TiO₂@FTO) *via* a hydrothermal

method. In a chemical solution, 15 mL of HCl was dissolved in 15 mL of deionized (DI) water, followed by stirring for 10 min. After stirring, 2 mL of titanium butoxide was added dropwise in the solution using a capillary tube and stirred the solution for 1 h to make a homogenous solution of the precursors present in an aqueous medium. Then, the as-prepared solution and the FTO substrate were placed in a Teflon liner stainless steel autoclave, where the conductive side of the FTO substrate was facing down. The hydrothermal process was conducted by putting the autoclave in an oven at 180 °C for 5 h for the nucleation of the precursor on the substrate geometry. Further, the autoclave was cooled down to room temperature, and then, a white thin film-deposited FTO substrate was obtained and rinsed with DI water, and dried at 180 °C for 2 h. Afterwards, the as-prepared sample was taken for further characterization to check the phase and purity of the deposited material. Surface morphology of the as-prepared sample has been studied using a scanning electron microscope (Supra Zeiss 55, FESEM). The crystal structure of the samples was examined by X-Ray diffraction (XRD) using an X-Ray diffractometer (D8 Advance, Bruker) with Cu K_α radiation ($\lambda = 0.154$ nm). The TD Raman data from the sample have been recorded in the automatic mode using the software control attached with a Raman spectrometer (Horiba Jobin-Yvon) with a 633 nm laser. The temperature has been controlled through a Linkam Stage attached with appropriate interfacing to the Raman spectrometer software (LabSpec).

Results and discussion

Surface morphology and microstructure of the TiO₂@FTO sample prepared *via* a hydrothermal method were studied *via* SEM, and the obtained images were analyzed using the ImageJTM software. The SEM images (Fig. 1) show that a uniform deposition has taken place. The top view SEM micrograph indicates that the sample contained well-aligned rod-like structures. This has been examined using the surface profile obtained by the ImageJ software (inset, Fig. 1a), which shows rod-like structures. A few hundred nanometers thick rods were visible when seen at the higher magnification SEM image (Fig. 1b). The average thickness of the rods was found to be ~220 nm as obtained from the line profiling (inset, Fig. 1b)

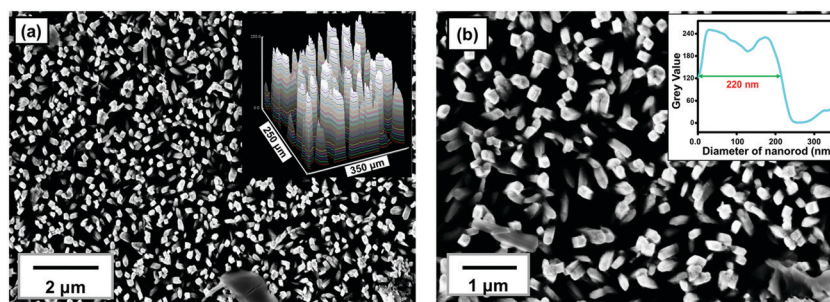


Fig. 1 (a and b) Top view of the SEM image of TNRs of the rutile phase deposited on the FTO substrate at different magnifications. Corresponding surface profile and line scan plots are shown in the corresponding insets, respectively.



performed on the SEM image. Further, phase and structural studies on the as-prepared thin film have been carried out *via* XRD and Raman spectroscopy.

The XRD pattern (Fig. 2a) showed several diffraction peaks at 2θ values of 27° , 36° , 39° , 41° , 44° , 54° , 57° , 64° and 69° . The peaks in the diffraction pattern with the corresponding (hkl) planes (Fig. 2a) can be identified as originating from the rutile phase of TiO_2 ^{55,56} (marked with *) and the FTO substrate⁵⁷ (marked as #). Since, TiO_2 is known to have defects because of the oxygen vacancy where an O^{2-} ion moves from a normally occupied lattice site to a vacant interstitial site which is supposed to be prevalent defect in many metal oxides. Under thermal conditions, hydrogen atom interacts with the lattice oxygen of TiO_2 on the surface, which results in the formation of oxygen vacancies, and changes the surface properties of TiO_2 .^{58,59} No such defects can be identified from the XRD pattern in the present sample.

Furthermore, no additional peak or hump is seen in the XRD, which revealed that pure single phased TNRs have been fabricated. To confirm the phase of the TNRs, Raman spectroscopy has been carried out (Fig. 2b), which shows four Raman active modes at 143 cm^{-1} , 235 cm^{-1} , 447 cm^{-1} and 610 cm^{-1} at room temperature, corresponding to the B_{1g} (143 cm^{-1}), E_g (447 cm^{-1}) and A_{1g} (610 cm^{-1}) modes of the rutile TNRs.^{60–62} The peak appears at 235 cm^{-1} , which arose due to the multiphoton process in the rutile TNRs.⁶³ These three different vibration bands of Ti^{4+} and O^{2-} atoms at their respective position also confirms the tetragonal crystal structure of rutile TiO_2 , making it consistent with the XRD results. It is known that these Raman active modes in TiO_2 are comprised of motions of O^{2-} ions with respect to the central stationary Ti^{4+} ions, either perpendicular to the c -axis, which is attributed to the A_{1g} and B_{1g} modes, or along to c -axis, which is attributed to the E_g mode. It is clear that the E_g and A_{1g} Raman modes are as usual most intense modes, and B_{1g} is the weakest one. The structural and spectroscopic analysis mentioned above (Fig. 1 and 2) reveal that the deposited film contains $\sim 220\text{ nm}$ thick TNRs in the rutile phase, and has been studied further *via* TD Raman spectroscopy and thermal mapping.

As mentioned above, possible anharmonic effects in Raman modes have been studied using TD Raman spectromicroscopy. The TD Raman spectra of rutile TNRs have been recorded in the temperature range of $300\text{--}725\text{ K}$ and analyzed accordingly. Fig. 3a shows the Raman spectra from rutile TNRs at various temperatures, plotted with an axis-offset for better visibility. A TD phonon softening could be seen very clearly in the E_g mode, whereas the A_{1g} mode remained immune to the thermal effects in terms of its peak position. For better appreciation of the TD Raman modes, it has also been displayed in the form of a Raman thermal image (Fig. 3b). For better clarity, the thermal map of the E_g mode has been zoomed in (Fig. S1, ESI[†]), showing the phonon softening and varying width of the Raman mode.

The thermal immunity of the B_{1g} and A_{1g} modes was caused by the fact that the shifts due to thermal expansion and higher order anharmonicities were complementary to each other to compensate each other, which is well known for TNRs, as reported by Samara and Peercy.⁶⁴ On the other hand, as mentioned above, the most intense E_g mode underwent a phonon softening of $\sim 22\text{ cm}^{-1}$ ($\Delta\omega$) for a temperature gradient (ΔT) of 475 K . The likely reason for the phonon softening is the temperature-induced thermal expansion, which decreases the vibrational frequency.^{49,65,66} By a careful observation, one can notice an increasing spectral width (measured in terms of full width at half maxima or FWHM) with the increasing temperature (Fig. 3). Since the FWHM is a measure of phonon lifetime, an increasing FWHM with the increasing temperature indicated that the phonon lifetime reduced at elevated temperatures. This hinted towards a faster phonon decay at higher temperatures and can be understood using a theoretical framework as follows.

Looking at the indicative TD phonon softening and phonon life time variation of the E_g Raman mode of TNRs, anharmonicity has been analyzed within the theoretical framework of the Balkanski's anharmonic model.⁴⁹ As per the model, at high temperatures, an optical phonon decays into two or three phonons, thus decreasing the phonon life time, which is manifested as a larger Raman spectral width (FWHM). The presence of anharmonicity

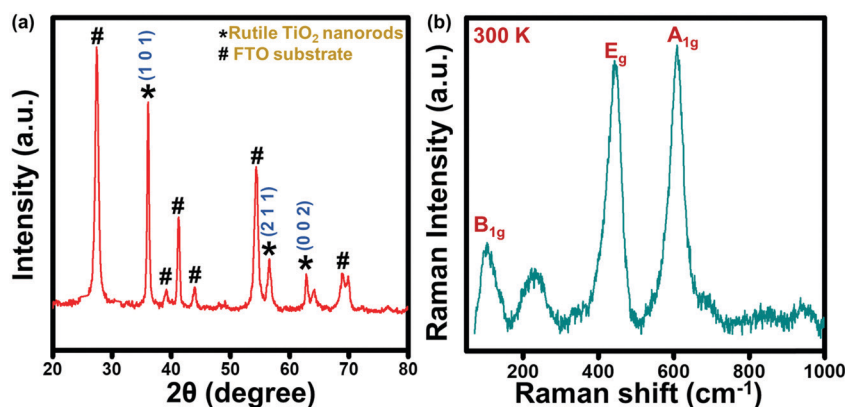


Fig. 2 (a) X-Ray diffraction pattern of rutile TiO_2 nanorods deposited on the FTO substrate with the corresponding (hkl) plane (b) The experimental Raman spectrum of rutile TiO_2 nanorods at room temperature (300 K).





Fig. 3 (a) Temperature-dependent experimentally observed Raman spectra from rutile TNRs and (b) the corresponding thermal Raman image for E_g and A_{1g} Raman modes.

forces the phonons to oscillate with a lower frequency, and gets identified through the Raman peak (red) shift. This decay of optical phonons into two or three phonons is represented mathematically as cubic or quartic anharmonicities. Hence, in this simplified model, the TD Raman peak position (eqn (1) and (2)) and spectral linewidth (FWHM) are given as eqn (3) and (4):

$$\omega(T) = \omega_0 + \Delta\Omega(T) \quad (1)$$

$$\Delta\Omega(T) = A \left[1 + \frac{2}{e^x - 1} \right] + B \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right] \quad (2)$$

$$\Gamma(T) = \Gamma_0 + \Delta\Gamma(T) \quad (3)$$

$$\Delta\Gamma(T) = C \left[1 + \frac{2}{e^x - 1} \right] + D \left[1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right] \quad (4)$$

where ω_0 ($= 447 \text{ cm}^{-1}$) and Γ_0 ($= 35 \text{ cm}^{-1}$) are the Raman peak position and spectral linewidth of rutile TNRs, respectively, at room temperature (taken as the reference). Here, the terms $\Delta\Omega(T)$ and $\Delta\Gamma(T)$ are the anharmonicities in Raman shift and Raman linewidth, which arise due to temperature. The first

terms in eqn (2) and (4) describe the coupling of two optical phonons to lower energy phonons (three phonon coupling and cubic anharmonicity), which is proportional to T at higher temperatures, whereas the second terms in eqn (2) and (4) describe the four phonon coupling, (quartic anharmonicity), which is proportional to T^2 at higher temperatures according to the Balkanski anharmonic model. The experimentally observed the TD Raman peak position (ω) and spectral linewidth (Γ) variation has been correlated with the values estimated using eqn (1) and (3) to check the correlation between the above-mentioned hypothesis of the TD variations in Raman spectral parameters (Fig. 4).

The calculated Raman shift (Fig. 4a) and linewidth (Fig. 4b) by considering the anharmonic effects (eqn (1)–(4)) are represented by solid lines, whereas the discrete points show the values obtained from the experimental Raman data for the E_g mode. The solid line in Fig. 4a has been obtained using A and B as the fitting parameters, which shows the best fit with the experimental data (solid black points) when the values of $A = -0.50 \text{ cm}^{-1}$ and $B = -0.85 \text{ cm}^{-1}$ are used. These values



Fig. 4 Variation in the Raman peak position (a) and FWHM (b) as a function of temperature where solid lines represent the curve predicted by the Balkanski model and discrete points correspond to the experimental data.



for silicon, used by Balkanski *et al.*, came out to be -4.24 cm^{-1} and -0.174 cm^{-1} . A good fit between the experimental and theoretical (using both the decay terms, eqn (2)) values in Fig. 4a indicates that the E_g Raman mode redshift from 447 cm^{-1} to 422 cm^{-1} with an increase in the temperature from 300 K to 725 K, strongly suggesting that anharmonicity is caused by both cubic and quartic anharmonicities. It is worth mentioning that the role of the confinement effect has not been considered here because its effect on the mode vibrational energy and thus Raman peak position for the rutile phase is not significant enough, as reported by T. Mazza *et al.*⁶² Alternatively, the total Raman peak shift in the E_g mode is solely because of the anharmonic effect. A similar theoretical analysis has also been done for the Raman spectral width (Fig. 4b) using eqn (3) and (4). The best fit between the experimental data (discrete points, Fig. 4b) and theoretical values (solid line, Fig. 4b) are obtained for the values of $C = 2.3\text{ cm}^{-1}$ and $D = 0.42\text{ cm}^{-1}$ (anharmonic parameters). These values for silicon, used by Balkanski *et al.*, came out to be 1.295 cm^{-1} and 0.105 cm^{-1} , respectively. The FWHM of the E_g mode increased from 41 cm^{-1} to 60 cm^{-1} (Fig. 4b) due to the anharmonic effect, which was caused by phonon softening at high temperatures (300–725 K).

Unlike the E_g Raman mode, the A_{1g} mode did not undergo anharmonic effects, making it immune towards the thermal effects, which indicate that the thermal expansion was small enough to keep the corresponding mode to vibrate in the harmonic regime. This is reflected as the temperature-independent Raman peak position of this mode. On the other hand, the FWHM of the A_{1g} mode varied only between 40.5 cm^{-1} and 67 cm^{-1} in the temperature range of 300–725 K, which meant that, though the vibrations remained harmonic, it still suffers a phonon decay, thus decreasing the phonon lifetime with the increasing temperature. Observed temperature-dependent width and estimated phonon life time of the A_{1g} mode have been provided in Fig. S2 and S3 (ESI†). Alternatively, E_g and A_{1g} vibrational modes of rutile TNRs behaved differently under the influence of thermal perturbations. At the nanoscale, the E_g Raman mode of rutile TNRs exhibited a redshift and broadening up to a few cm^{-1} , but while applying an anharmonic effect to the system, these changes in Raman parameters are huge and are of great interest. Due to the phonon anharmonicity, one optical phonon decays into two or three phonons, which affects each Raman mode differently and can be explained successfully using the existing Balkanski model as evident from the consistency between the experimental Raman data and theoretically obtained values.

Conclusion

Temperature-dependent Raman spectroscopy and Raman thermal mapping of rutile TiO_2 nanorods revealed that the E_g mode responded anharmonically to the thermal perturbations at higher temperatures (more than room temperature), whereas the A_{1g} mode was immune to such a temperature rise. A direct

proportionality between the phonon mode frequency and temperature was observed due to anharmonic vibrations of this mode. In addition, the phonon lifetime decreases with the increase in temperature, indicating that hot phonons decay faster. This has been concluded because the experimental observations were consistent with the established phonon decay model. The model, when two- (three-) phonon decay of optical phonon were considered, showed a good agreement with the experimental observation for the E_g mode. On the other hand, however, the A_{1g} mode frequency is immune to thermal perturbations, a little change in the lifetime is observed. The mode-dependent anharmonicity is associated with the vibration-dependent polarizability for a given mode. Overall, temperature-dependent Raman spectromicroscopy helps in getting a consolidate insight about anharmonic response of different Raman active modes from rutile TiO_2 nanorods.

Conflicts of interest

There are no conflicts to declare.

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