Determination of surface oxygen vacancy position in SnO$_2$ nanocrystals by Raman spectroscopy

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**ABSTRACT**

Raman spectra acquired from SnO$_2$ nanocrystals with different sizes show a size-independent Raman mode at $\sim$574 cm$^{-1}$. The intensity increases as the nanocrystal size decreases and this tendency is contrary to that of the normal bulk Raman modes. By considering the existence of oxygen vacancies at the nanocrystal surface, we adopt the density functional theory to calculate the Raman spectra with different oxygen vacancy positions and concentrations. The results clearly demonstrate that the in-plane oxygen vacancy is responsible for the 574 cm$^{-1}$ mode and the intensity enhancement is a result of the higher in-plane oxygen vacancy concentration.

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Tin oxide (SnO$_2$) is one of the most attractive nanostructures due to its interesting fundamental physical properties [1–3] and promising applications in new-generation, high-performance devices such as batteries, gas sensors, catalysts, and biosensors [4–6]. Many SnO$_2$ nanostructures with different morphologies such as nanowires (nanorods) [7], nanoribbons (nanobelts) [8,9], and nanocrystals [10,11] have been fabricated to investigate their physical properties and applications. Oxygen vacancies (OVs) which commonly exist on the surfaces of transition metal oxides [12,13] are known to play a critical role in applications to heterogeneous catalysis, photoelectrolysis, and biomedical engineering. However, the roles of OVs are sometimes controversial due to the complexity of the microscopic details. A typical example is the origin of the size-independent Raman mode at $\sim$574 cm$^{-1}$ frequently observed from SnO$_2$ nanostructured materials. This mode was initially considered to be due to vacant lattice sites and local lattice disorders in the interface components [14]. Further studies on the Raman spectra of the SnO$_2$ NCs annealed at different temperatures in O$_2$ and vacuum suggested that the vacant lattice sites might be oxygen deficiencies [15]. However, other experiments suggested that the size-independent Raman mode did not occur in SnO$_2$ ($x < 2$) NCs [16]. These conflicting results add to the mystery and so it is important to clarify the mechanism.

It is well known that SnO$_2$ NCs grow when annealed and their internal and surface structures change inevitably. Hence, the origin of the 574 cm$^{-1}$ Raman mode cannot be unequivocally identified by simply examining the Raman spectra obtained from samples after various thermal treatment steps. In this work, we hydrothermally synthesize SnO$_2$ NCs with different sizes and then carefully examine the dependence of the Raman mode on the NC size. It is found that the frequency is not related to the NC size, but its intensity increases with decreasing NC size. To explain the experimental results, we use the density functional theory (DFT) to calculate the influence of the OVs at the bridging, subbridging, and in-plane positions of the NC surface on the Raman spectra. The results indicate that the 574 cm$^{-1}$ Raman mode depends strongly on the formation of OVs in the in-plane positions at the NC surface and its intensity enhancement is due to increased OV concentration. This work improves our understanding of the OV properties in SnO$_2$ and is beneficial to further applications.

The preparation process of small agglomerated spherical SnO$_2$ NCs has been described previously [17]. 2.8 g SnCl$_4$·5H$_2$O and suitable aqueous ammonia were used for synthesis in a 120 ml closed cylindrical Teflon-lined stainless steel autoclave filled with deionized water, followed by ultrasonic vibration and heating for 24 (sample A), 12 (sample B), and 2 h (sample C) at 200 °C. The white precipitates were centrifuged and thoroughly rinsed with water and ethanol several times. They were then put on a Si (110) substrate and dried at 40 °C in an oven. The morphologies were observed by high-resolution transmission electron microscopy.
The Raman spectra of three samples A–C are presented in Fig. 2(a). Except for the well known $A_{1g}$ mode whose intensity increases with NC size, a broad Raman peak (labeled as $A_s$) appears at 574 cm$^{-1}$ from all the samples. Its peak position is independent of the NC size, but its intensity increases with decreasing NC size. This indicates that the 574 cm$^{-1}$ mode arises either as a consequence of increase in the surface-to-volume atom ratio or due to conversion from crystalline to amorphous induced by increasing disordered atoms [14]. However, all the nanoparticles are crystalline according to the HR-TEM images in Fig. 1(b). This suggests that the Raman mode does not correspond to the 566 cm$^{-1}$ one which occurs in amorphous SnO$_2$ films as the amorphous component [14]. Hence, a specific surface structure may be responsible for this mode. It is well known that a common NC always has a crystalline core and surface component and some OVs commonly exist in the surface layer [15]. The surface region increases as the NC size decreases and so it is possible that the mode intensity enhancement is due to increased OV concentration in the surface region. To prove this hypothesis, the integrated intensity ratio $\rho$ of modes $A_s$ to $A_{1g}$ is presented in Fig. 2(b). The ratio of the core and surface layer volumes corresponding to the ratio $\rho$ of the Raman scattering intensities by each component can be described as $\rho \propto K[(\frac{r}{d})^3 - 1]$ where $r$ is the NC radius and $d$ is the surface layer thickness. When the NC size is reduced, the volume occupied by the surface component increases compared to that occupied by the core component. In our calculations, parameters $d$ and $K$ are taken from previous literature to be 1.12 nm and 2.15 nm [19,20]. In the extreme case of a single SnO$_2$ crystal, surface reconstruction in the (110) surface involves up to three monolayers of atoms which have OVs. This gives rise to a nonstoichiometric SnO$_x$ at the surface layer. Such a surface layer has OVs at three different positions.

To disclose the dependence of the $A_s$ mode on OV positions, the calculations are done on density functional theory (DFT) in the PBE generalized gradient approximation using the CASTEP package with a plane-wave norm-conserving pseudopotential [21]. An energy cutoff of 450 eV is used for expanding the wave functions and a Monkhorst–Pack $k$-points grid is $4 \times 8 \times 4$ for the bulk structure and $2 \times 4 \times 1$ for the surface, which have been tested to converge. The rutile SnO$_2$ surface consisting of a six trilayer...
Fig. 3. (Color on-line) (a) Calculated Raman spectra of the Sn$_{12}$O$_{23}$ supercell with bridging (line b), subbridging (line c), and in-plane OV (line d), respectively. The Raman spectrum of the supercell without OV is shown (line a) for comparison. (b) Calculated Raman spectrum of the Sn$_{12}$O$_{23}$ supercell with two in-plane OVs (line e). Lines a and d are consistent with those in (a).

slab and a 1.2 nm vacuum thickness is modeled. The two bottom
trilayers are fixed to mimic the bulk, and relaxation is carried out
until SCF tolerance converges to 2.0 × 10$^{-6}$ eV/atom. A
typical schematic of the optimized rutile SnO$_2$ surface is inserted
in Fig. 2(b) in which the stoichiometric (110) surface is characterized
by bridging, subbridging, and in-plane oxygen atoms, and the
top face of the supercell illustrates such a surface terminated by
bridging oxygen atoms.

To compare the Raman spectra from surfaces with different
OV positions, a Sn$_{12}$O$_{23}$ supercell with a bridging, a subbridging,
or an in-plane OV, respectively is constructed and calculated. The
obtained spectra are presented in Fig. 3(a). The corresponding
result from the Sn$_{12}$O$_{23}$ supercell without OV is also shown
for comparison. We can see that with the presence of different OVs,
the $A_s$ mode shows different position and intensity. The OV in a
bridging (line b) or subbridging (line c) position cannot effectively
yield the Raman mode at $\sim$574 cm$^{-1}$, which is similar to that
without OV (line a). Therefore, it is inferred that the in-plane OV
(line d) is responsible for the $A_s$ mode. In the current samples,
other OVs may also exist simultaneously but they do not induce
the observed experimental result. Comprehensive first-principle
calculations on the strained rutile structure indicate that the
formation of different types of OVs strongly depends on external
strain [22]. In the synthesis at 200 °C, water molecules evaporate
to change the pressure in the autoclave and the in-plane OVs
are formed. Hence, it is reasonable to infer that the fact that
the $\sim$574 cm$^{-1}$ Raman mode is not observed in some previous reports
should be due to the different OV positions as a result of different
preparation conditions [16,23–25].

With decreasing NC size, the intensity ratio of modes $A_s$ to $A_{1g}$,
$\rho$, increases due to the increased surface-to-volume atom ratio.
With respect to the OV formation at the surface, the energetically
favorable in-plane OVs easily appear on the surface of small
NCs with a large surface-to-volume atom ratio [22], thus the
in-plane OV concentration increases on small NCs. To support our
assessment, the same periodic Sn$_{12}$O$_{22}$ supercell with two in-
plane OVs is constructed and calculated. The corresponding Raman
spectrum is presented in Fig. 3(b) (curve e). It can be seen that
the $A_s$ mode intensity increases with increased OV number and
the intensity of the shoulder peak in the high-frequency side
decreases, which is in good agreement with our experimental
observation [Fig. 2(a)]. Thus, we can conclude that the in-plane OVs
may indeed be responsible for the size-independent Raman mode
at $\sim$574 cm$^{-1}$. Here, we would like to point out that the lineshape
difference between the calculated and experimental spectra may
be because we only use an ideal rutile Sn$_{12}$O$_{24}$ supercell for the
DFT calculation and the effect of the surface atom disorder has not
been considered. Since the DFT cannot describe the linewidth
of the Raman mode, more work is under way.

In summary, we have examined the Raman spectra of the
SnO$_2$ NCs with different sizes fabricated by the hydrothermal
method and found that with decreasing NC size, the Raman
mode at 574 cm$^{-1}$ does not shift in frequency but increases
in intensity. Considering the existence of OVs at the NC surface
and the higher OV concentration in smaller NCs (larger surface-to-
volume atom ratio), we adopt the DFT to calculate the Raman
spectra with different OV positions and concentrations. The results
clearly indicate that the expected effects of in-plane OVs are
consistent with the experimental spectral features and nanocrystal
size dependence of the 574 cm$^{-1}$ mode. Its intensity enhancement
is a result of the higher in-plane OV concentration. The results
provide good insight into the influence of OVs on the Raman
behavior in SnO$_2$ nanostructured materials.

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References