Electronic states and photoluminescence of TiO\textsubscript{2} nanotubes with adsorbed surface oxygen


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The electronic states associated with enhanced photocatalytic activity of anodic anatase TiO\textsubscript{2} nanotubes (NTs) annealed in N\textsubscript{2} and O\textsubscript{2} are investigated by photoluminescence (PL). The NTs annealed in N\textsubscript{2} show a green peak related to oxygen vacancies and its position blueshifts with deceasing temperature, whereas those annealed in O\textsubscript{2} show a double peak at 475–600 nm and the energy separation increases with decreasing temperature. Spectral analysis and density function theory calculation disclose that the double peak results from residual oxygen vacancies and oxygen atoms on the NT wall and the increased energy separation arises from the larger difference between the inner and outer NT stress at low temperature. © 2012 American Institute of Physics.

[Ti oxide nanostructures have attracted much attention because of their interesting applications such as gas sensing, solar-to-chemical conversion (water splitting), and environment cleaning (photodecomposition of harmful materials or dirt)]. The properties depend very much on the surface structure and reactant adsorption. Nanostructures such as nanotubes (NTs), nanocrystals (NCs), nanodisks, and nanowires have been fabricated and their optical and electronic characteristics and potential applications have been explored. The NT structures with a large surface to volume ratio tend to yield excellent performance. TiO\textsubscript{2} has three common phases, namely, anatase, rutile, and brookite. Anatase and rutile are more relevant to many applications and between the two, anatase TiO\textsubscript{2} has attracted more interest especially in surface chemistry due to its higher catalytic activity.

In many energy and environment related applications, improved efficiency and stability are required and a better understanding of the related mechanism is thus crucial. It has been shown that oxygen adsorption onto the nanostructure surface can effectively modify the reaction captivity and, therefore, it is important to clarify the oxygen mechanism. However, the complexity of the nanostructure and lack of systematic theoretical assessment make it challenging. Photoluminescence (PL) can reflect the interaction between the electronic states of a nanostructure with vacancy structure and adsorptive reactants and there has been extensive research to identify its origin. The sensing properties of TiO\textsubscript{2} are generally based on sensitive transduction of the gas/surface interaction (adsorption or catalytic oxidation) into electrical conductivity. If the PL origin of the nanostructure with adsorptive oxygen can be identified experimentally and theoretically, this mechanism can be applied to oxygen sensing by simply analyzing the PL spectral change. In this respect, the low-temperature PL spectral changes in anatase TiO\textsubscript{2} NTs with a vacancy structure and adsorbed oxygen should be clarified. The objective of this work is to identify and explain the PL properties of the TiO\textsubscript{2} NTs formed by anodic oxidation with both vacancy structure and oxygen adsorption to develop potential catalytic and sensing applications.

The TiO\textsubscript{2} NTs were formed by anodic oxidation of a Ti foil at 30 V and 10 °C in an ethylene glycol solution containing NH\textsubscript{4}F (0.5 wt. %) for 5 h. The sample was annealed in O\textsubscript{2} or N\textsubscript{2} at T\textsubscript{an} = 400 °C for 30 min. The samples were characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) (JEOL-2100), electron paramagnetic resonance (EPS) spectroscopy, UV-visible diffuse reflection spectroscopy (DRS), x-ray diffraction (XRD), PL excitation spectroscopy, and x-ray photoelectron spectroscopy (XPS). All the measurements were conducted at room temperature.

The SEM image acquired from the NT samples annealed at 400 °C in O\textsubscript{2} for 30 min is shown in Fig. 1(a), and the orderly self-organized NT array can be clearly observed. The average NT outer diameter (marked by blue dashed lines) is about 83 nm and the NT wall thickness (marked by black dashed lines) is approximately 8.5 nm. To clearly display this NT morphology, lateral SEM image of the NT array is shown in Fig. 1(b) and the length of the NTs is about several micrometers. Obviously, the huge internal space of the NTs can be effectively used for oxygen adsorption and sensing.

To further investigate the microstructures of the NTs, the electron diffraction pattern of the TiO\textsubscript{2} NTs showing the (004) is shown in Fig. 2(a) and compared to the JCPDS card data. An important difference is that the strongest diffraction peak of the TiO\textsubscript{2} NTs arises from (004) instead of (101) which is common in anatase TiO\textsubscript{2}. It can be understood...
to be the dominant exposed (001) facet on the NT surface. The UV-visible DRS result is shown in the inset of Fig. 2(b).\textsuperscript{15} By plotting the Kubelka-Munk function versus wavelength,\textsuperscript{16} the bandgap of the anatase TiO\textsubscript{2} NT is derived to be about 3.38 eV (Fig. 2(b)), which is slightly larger than that of bulk TiO\textsubscript{2} (3.2 eV). In the anatase TiO\textsubscript{2} nanoparticle system, it has been reported that the excition Bohr radius R is about 0.8 nm and no shift in the bandgap energy has been observed for nanoparticles with a size of $2R \geq 1.5$ nm.\textsuperscript{17} Therefore, this enlarged bandgap (3.38 eV) cannot simply be ascribed to quantum confinement in the TiO\textsubscript{2} NT, but rather it may originate from the NT adsorptive characteristics. The EPR spectrum in Fig. 2(d) indicates that electrons of the adsorbed oxygen atoms can be trapped by Ti$^{4+}$ atoms on the NT wall to form the Ti$^{3+}$ valence state. This changes the effective electron and hole masses and consequently causes a slight bandgap expansion of the NTs.\textsuperscript{18–20} The Ti 2p XPS spectrum in Fig. 2(c) reveals that the binding energies of Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ are 459.2 and 465.1 eV, respectively. Compared to the binding energy of Ti$^{4+}$ in pure anatase TiO\textsubscript{2} (458.6 eV), there is a shift of 0.6 eV, suggesting that some Ti$^{3+}$ or Ti$^{2+}$ still exist in the sample.\textsuperscript{21,22} Therefore, this enlarged bandgap (3.38 eV) cannot simply be ascribed to quantum confinement in the TiO\textsubscript{2} NT, but rather it may originate from the NT adsorptive characteristics. The EPR signal is shown in Fig. 2(d). The Lande g value is obtained to be 2.0056 and larger than that of the sample with only OVs ($g = 2.003$).\textsuperscript{22,23} Because the anion radicals $O_2^-$ and/or $O^-$ can be formed due to capture of thermally generated electrons and holes by adsorbed oxygen ($O_2^- + e^- \rightarrow O_2^-$) during annealing, the concentration of $O_2^-$ increases with adsorptive oxygen on the anatase TiO\textsubscript{2} surface. This makes the g factor larger.\textsuperscript{23} The above analysis shows that the synthesized NTs have the anatase phase with a certain OV amount and meanwhile the NT walls are covered by adsorbed oxygen atoms.

Figure 3(a) shows the temperature-dependent PL spectra acquired from the anatase TiO\textsubscript{2} NTs annealed at 400°C in N\textsubscript{2} excited by the 320 nm line of a xenon lamp. All the spectra show a visible green band at $\approx 515$ nm (2.41 eV) which has been assigned to OVs that are essential defects in metal oxides.\textsuperscript{24,25} Its intensity increases gradually as the measurement temperature decreases due to weaker...
A gradient approximation is employed to describe the conserving pseudopotential is used for the electron-ion interactions. Films are carved along the (001) planes. The norm-wise TiO$_2$ film to investigate the effects of the internal OVs and oxygen adsorption under different applied stresses.

Confined TiO$_2$ film with OVs and oxygen adsorption under different applied stresses. The difference in the applied stress caused by oxygen adsorption on the inner and outer NT surfaces increases as the measurement temperature decreases and it can cause the double-peak PL. The difference in the applied stress caused by oxygen adsorption on the inner and outer NT surfaces increases as the measurement temperature decreases and it causes increased splitting and shifting of the PL peak.

To understand the origin of the double-peak PL, we perform a density functional theory (DFT) study on the anatase TiO$_2$ films with (001) surface and with different OVs and oxygen adsorption. The specific contribution of the complex surface states to electron-hole recombination can be investigated by computing the optical transition matrix element associated with surface states, which is defined as $|P|^2 = \sum_{E'} |\langle \Psi_{E'}^b(\mathbf{r}) | \mathbf{u}_i | \Psi_E^c(\mathbf{r}) \rangle|^2 \delta(E_E' - E_{E'} - E)$, in which $E$ is the transition energy, $k^-$ is the Bloch wave vector of the superlattice, $E_{E'}$ and $|\Psi_{E'}^c(\mathbf{r})\rangle$ are the eigen-energy and wave function of the state in the conduction, respectively, $\mathbf{r}$ is the position vector, and $\mathbf{u}$ is the unit vector along the unpolarization of the light. As the measurement temperature decreases, the applied stress in the calculated models increases and it can be defined as $\varepsilon = (a(a - a_0))/a_0$, and $a$ and $a_0$ are the stressed and unstressed lattice constants.

Based on the model shown in Fig. 1(c) (only including OVs), the calculated averaged $|P|^2$ values are shown in Fig. 4(a). As the OV density increases from $x = 0.0$ to $x = 0.2$, an obvious peak (S) begins to appear at ~545 nm and then upshifts to 550 nm with increasing stress from $\varepsilon_1 = 0.00\%$ to $\varepsilon_2 = 0.29\%$, which is consistent with the experimental measurements shown in Figs. 3(a) and 3(b). After annealing in O$_2$, partial OVs are removed and superfluous oxygen atoms adsorb on the surface near the OV positions to construct Ti-O bonds forming a more stable stoichiometric NT surface, as shown in Fig. 1(d). In this case of OV density $x = 0.1$ and adsorbed oxygen atom density $y = 0.1$, the calculated $|P|^2$ values shown in Fig. 4(b) reveal that introduction of surface states originating from adsorbed oxygen atoms separates the PL spectrum into two $(S_1$ and $S)$. The energy separation between the two peaks increases with decreasing measurement temperature as a result of the larger difference between the inner and outer NT stresses, as shown in Fig. 3(c). The calculation suggests that surface oxygen adsorption changes the electronic structure and this may be responsible for the enhanced photocatalytic activity observed from annealed TiO$_2$ NT samples. The difference between the experimental and theoretical PL wavelengths can be ascribed to the sample complexity.

In conclusion, anatase TiO$_2$ NTs with OVs are synthesized by anodic oxidation and then annealed in N$_2$ or O$_2$. The
low-temperature PL spectra reveal a single peak from the NTs annealed in N\textsubscript{2} and a double peak for those annealed in O\textsubscript{2}. The energy separation between the two latter subpeaks increases as the measurement temperature decreases. Spectral analyses and theoretical calculation suggest that the double peak PL originates from both the residual OVs and adsorbed oxygen atoms on the NT wall and the increased energy separation is due to increased difference between inner and outer NT stresses during lower temperature measurement.

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