Figures 3a and 3b show that the stable zones of the 450 and 550 °C-annealed TiO_2 samples, which ~~contain~~consist of only or almost entirely ~~the~~ anatase nanotubes, ~~have~~had an O/Ti ratio of ~~about~~ 1.9-2.0. In contrast, Figures 3c and 3d show that the O/Ti ratio of the stable zones of the 650 and 750 °C-annealed ~~TiO_2~~ samples ~~is~~was significantly less than 2 (O/Ti ≈ 1.6-1.7). ~~For the 650 °C-annealed sample, the~~The stable zone ~~is~~ consisted of both ~~the~~ anatase nanotubes and rutile film~~, while~~ for the 650 °C-annealed sample, but was almost entirely rutile film for the 750 °C-annealed sample~~, almost entirely the rutile film.~~. Since secondary phases ~~are not detected by XRD~~ in the annealed ~~TiO_2~~ samples were not detected by XRD, an O/Ti ratio significantly less than 2 indicates a high concentration of oxygen vacancies in the stable zones of the 650 and 750 °C-annealed ~~TiO_2~~ samples. ~~The~~A direct relationship between ~~the~~ oxygen vacancy concentration and annealing temperature ~~is~~can be established based on analysis of the XPS ~~analyses~~data. The TiO_2 nanostructure can be seen as an oxide barrier between the annealing atmosphere (air) and Ti substrate, and ~~it is believed that~~ the diffusion of the oxygen atoms from the atmosphere into the oxide is believed to be slower than the diffusion of the oxygen ions within the oxide. At high annealing temperatures, ~~the~~ oxygen ions from the existing nanostructure diffuse ~~downward to~~towards the nanostructure/Ti substrate interface ~~for~~, causing the oxidation of Ti ~~(i.e., to form~~and forming new rutile crystals~~).~~. During this process, ~~the~~ oxygen is not replenished from the atmosphere at the same rate as it is consumed in the oxidation reaction. ~~The~~This difference in ~~the~~ oxygen diffusion rates ~~would~~ eventually ~~result to~~results in an oxygen--deficient TiO_2 nanostructure, as revealed by the 650 and 750 °C-annealed samples.

3.3. Optical absorption and band gap

The ~~measured~~ UV-Vis absorption spectra of the annealed TiO_2 samples are shown in Figure 6. ~~With increasing annealing temperature, the~~ The absorption edge of the TiO_2 is gradually blue-shifted with increasing annealing temperature, and a significant increase in the visible light absorption~~,~~ occurs, as indicated by the "rising tail" of the absorption curve in the long-wavelength range~~, is observed.~~. By taking the minimum absorbance as the cut-off baseline, a comparison between the areas under the absorption curves of the annealed ~~TiO_2~~ samples can be made at wavelengths longer than their absorption edges ~~can be made~~ (such an area of the 750 °C-annealed sample

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is shaded in Figure 6 as an example). It is evident that the areas of the 650 and 750 °C-annealed samples are considerably larger than those of the 450 and 550 °C-annealed samples. The ~~stronger~~increase in visible ~~light~~ absorption with higher annealing temperature is ~~attributed~~attributable to the ~~increase in the~~increased concentration of oxygen vacancies. Extra electron energy levels associated with ~~the~~ oxygen vacancies are introduced below the bottom of the TiO_2 conduction band (i.e., donor states), resulting in strong absorption across the visible ~~light~~ region.

~~First-principles~~*Ab initio* density functional theory calculations were performed to ~~calculate~~determine the optical absorption coefficients of two oxygen-deficient anatase structures: Ti_nO_{2n-1}, where n = 8, 16, and 32 (i.e., containing a single oxygen vacancy) and Ti_nO_{2n-2}, where n = 16, 32, and 36 (i.e., containing two oxygen vacancies), and the results are shown in Figure 7. The sizes of the supercells adopted are specified in the figure legends. By varying the supercell size and optimizing the structure geometry, the oxygen vacancy concentration in the anatase crystal ~~can~~could be changed (~~i.e.,~~a smaller ~~the~~ supercell~~,~~ gives a higher ~~the~~ concentration). The supercells chosen for the calculation correspond to ~~an~~ oxygen vacancy ~~concentration~~ concentrations in the range of 3.1 to 12.5%. The calculated absorption spectrum of the ~~perfect~~ anatase TiO_2 ~~crystal (~~primitive cell~~)~~ is also shown in Figure 7 for comparison ~~purposes~~. The exact ~~procedures of~~procedure behind the theoretical calculations will be detailed in another article by the authors [41]. Figure 7 shows that when the oxygen vacancy concentration is increased ~~by reducing the supercell size, the~~, absorption in the long-wavelength range is noticeably increased for both the Ti_nO_{2n-1} and Ti_nO_{2n-2} structures ~~is noticeably increased~~, especially at wavelengths ~~above~~greater than 450 nm. Based on the ~~direct~~ relationship~~, as established by the XPS analyses,~~ between ~~the~~ oxygen vacancy concentration and annealing temperature established by XPS, the simulated light absorption behaviors are in agreement with ~~the~~ experimental observations, and demonstrate the positive ~~effect of the presence~~impact of oxygen vacancies on ~~the improvement of~~ visible light absorption. The calculated spectra also predict a blue-shift in the absorption edge with the presence of oxygen vacancies.

The Kubelka-Munk function ~~is~~was adopted to convert the measured UV-Vis reflectance spectra of the annealed TiO_2 samples (R_{sample}) into the equivalent absorption spectra ~~by~~, using the reflectance of Ti (R_{Ti}) as a reference standard. The

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CHECK: Please check that this terminology is acceptable - first-principles calculations are often referred to as *ab initio*.