

# X-ray spectroscopic study of the electronic structure of visible-light responsive N-, C- and S-doped TiO<sub>2</sub>

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## Abstract

The electronic origins of the visible-light response of N-, C- and S-doped TiO<sub>2</sub> have been studied using X-ray absorption, X-ray emission, and X-ray photoelectron spectroscopies. New electronic states are observed in the bulk band gap, above the valence band edge of pure TiO<sub>2</sub>, which can be directly related to the visible-light absorption of the N-, C- and S-doped TiO<sub>2</sub> materials.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) has been the subject of extensive studies since the late 1960s, due to its various applications in pigments, photoconductors, dielectric materials, and photocatalysts [1–9]. The wider application of TiO<sub>2</sub> as a photocatalyst can be realized by expanding its UV or near-UV absorption properties into visible-light region [6–14]. Doping TiO<sub>2</sub> with different elements such as nitrogen (N), carbon (C), and sulfur (S) has shown promising results for visible-light photocatalysis [6–14]. Titanium nitride (TiN) and carbide (TiC) are both metallic conductors with partially filled bands at the Fermi level ( $E_F$ ) and—chemical bonds of simultaneously metallic, covalent, and ionic characters [15–21], while titanium sulfide (TiS<sub>2</sub>) is regarded as a semiconductor or semimetal [22,23], with a bandgap of about 0.9 eV [24]. It is known that TiN, TiC, and TiS<sub>2</sub> can be oxidized into TiO<sub>2</sub> via high-temperature sintering in air or oxygen [16–18]. It has also been reported that C- and S-doped TiO<sub>2</sub> can be formed by heating TiC [14,25] and TiS<sub>2</sub> powders [13,26] at high temperatures. The oxidation of these

materials provides an attractive technique to prepare doped TiO<sub>2</sub> with visible-light absorption.

The electronic structure of TiO<sub>2</sub> is well understood both theoretically and experimentally [15,27–37], and is characterized by a band gap located between the oxygen 2p valence band and the titanium 3d conduction band [27]. X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) are powerful element-specific probes of the electronic structure of materials, and have been applied extensively to study pure TiO<sub>2</sub> [15–21,24,27–38]. In XAS, a core-level electron absorbs an X-ray photon and is excited to an unoccupied state above  $E_F$  [15,17,27,37]. In XES, a valence band electron relaxes to a core hole created by the X-ray absorption process via the emission of an X-ray photon [15,19,31,35]. In X-ray photoelectron spectroscopy, a core-level electron is excited above the vacuum level by the incident light and the kinetic energy of the emitted electrons is recorded. XAS and XES spectra reflect the element specific conduction and valence band partial density of states (PDOS), respectively [39,40]. In contrast, XPS measures the total density of states (DOS) of the valence band, as well as the kinetic energy of the core-level electrons (thus, the binding energy of the core-level electrons can be derived) [16,20,37,41–44]. Thus, by combining XAS, XES and XPS results, a comprehensive understanding

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of the electronic structure of these materials can be achieved.

We report here an XES, XAS, and XPS study of the electronic structure of N-, C- and S-doped TiO<sub>2</sub>, as well as that of pure TiO<sub>2</sub>. We have observed occupied states in the bulk band gap for the doped materials. These states do not exist in pure TiO<sub>2</sub>, and are likely related to the visible-light properties of the doped oxides.

## 2. Experimental

The TiN, TiC and TiS<sub>2</sub> were purchased from Strem Chemicals as powders. The N-, C- and S-doped TiO<sub>2</sub> samples were prepared by oxidation of the above reagents at 1000 °C for 6 h in a quartz tube under atmosphere inside a Lindberg tube furnace with a digital temperature control unit. These samples were then allowed to cool, and doped TiO<sub>2</sub> was obtained. Pure TiO<sub>2</sub> was obtained by heating at 1000 °C for 6 h in air a TiO<sub>2</sub> powder prepared via a commonly used sol–gel method [45].

X-ray diffraction (XRD) patterns were obtained on a Philips PW 3710 X-ray powder diffractometer. The UV–vis reflectance spectra were measured on a Cary 50 UV–vis spectrometer with a reflectance unit.

The X-ray spectroscopic experiments were measured at the undulator beamline 7.0 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory with a spherical grating monochromator [46]. Ti 2p (L<sub>2,3</sub>) XES and O 1s (K<sub>α</sub>) XES spectra of these samples were recorded by using a Nordgren-type grating spectrometer [47]. The spectrometer was mounted perpendicular to the incoming photon beam in the polarization plane and the resolution was 0.3 eV and 0.4 eV, respectively, for Ti 2p and O 1s XES spectra. The monochromator was set to the excitation energies of 475 eV and 565 eV respectively, for Ti 2p and O K<sub>α</sub> spectra with a resolution of 0.5 eV. The samples were mounted to have a beam incidence angle of 30° to sample surface. For energy calibration of the Ti 2p XES and O K<sub>α</sub> XES, the spectra of the reference samples Ti, TiO<sub>2</sub>, and Zn were measured. The base pressure of the chamber was  $2 \times 10^{-9}$  Torr. The absorption spectra at the Ti 2p and O 1s edges were measured by means of total electron yield (TEY) and with a monochromator resolution set to 0.2 eV. The absorption intensity was normalized by the current from a clean gold mesh placed in the incoming beam to compensate for fluctuations of the incoming photon intensity. The XES and XAS spectra were brought to a common energy scale using an elastic peak in the emission spectra recorded at the excitation energy set at the absorption edge. The measurement depth of XAS is normally around 10 nm, and is around 100 nm for XES.

For XPS measurements, a Perkin-Elmer PHI 5600 XPS System was used. The energy resolution of the spectrometer was 0.3–0.5 eV. Samples for XPS measurement were coated on carbon tape attached to the sample holder. The charge compensation was applied to each sample to the characteristic peak at 284.6 eV of the carbon tape. The pressure in the vacuum chamber during the measurements was below  $3 \times 10^{-10}$  Torr. The XPS data were taken with a monochromated X-ray source (Al K<sub>α</sub>). Ar<sup>+</sup> was applied to sputter the surface of the samples.

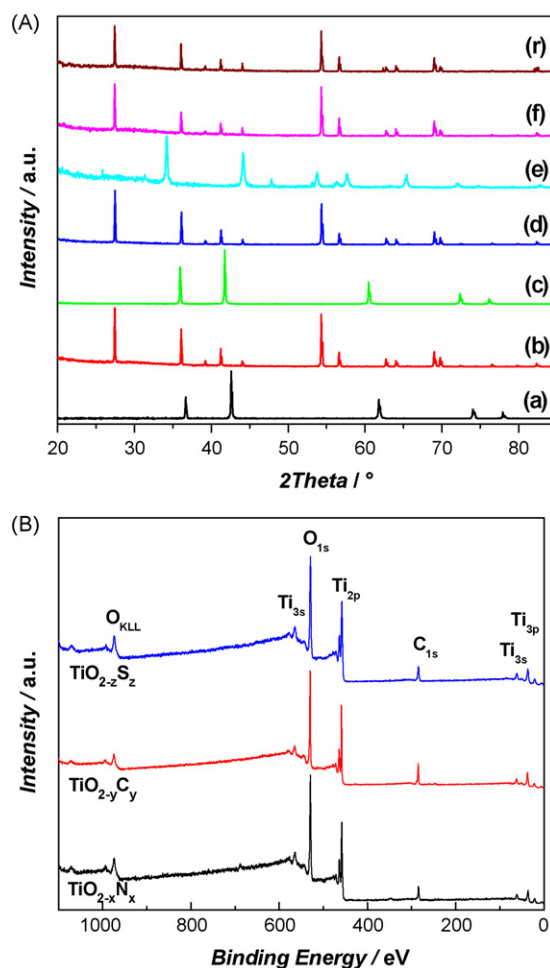


Fig. 1. (A) XRD patterns for the titanium compounds: (a) TiN; (b) TiO<sub>2-x</sub>N<sub>x</sub>; (c) TiC; (d) TiO<sub>2-y</sub>C<sub>y</sub>; (e) TiS<sub>2</sub>; (f) TiO<sub>2-z</sub>S<sub>z</sub>, and (r) pure rutile TiO<sub>2</sub>. The TiO<sub>2-x</sub>N<sub>x</sub>, TiO<sub>2-y</sub>C<sub>y</sub> and TiO<sub>2-z</sub>S<sub>z</sub> display the typical diffraction pattern of rutile TiO<sub>2</sub>. (B) Before Ar sputtering, wide energy range XPS of TiO<sub>2-x</sub>N<sub>x</sub>, TiO<sub>2-y</sub>C<sub>y</sub> and TiO<sub>2-z</sub>S<sub>z</sub>. The carbon 1s signals at 284.6 eV in the spectra were from the carbon tape.

## 3. Results

### 3.1. Structural, chemical and optical properties of N-, C- and S-doped TiO<sub>2</sub> as compared to pure TiO<sub>2</sub>

TiN and TiC have NaCl-like cubic structures, with N or C atoms occupying interstitial positions in a close packed arrangement of Ti atoms [21]. TiS<sub>2</sub> has a CdI<sub>2</sub>-like layered structure consisting of S–Ti–S slabs [24,38,48], with the Ti ions in a regular octahedral coordination to the sulfur ions [38]. The XRD in Fig. 1A shows that after heating treatment TiN, TiC and TiS<sub>2</sub> changed into TiO<sub>2</sub>-rutile phase. We designate the resultant samples after heating TiN, TiC and TiS<sub>2</sub> as TiO<sub>2-x</sub>N<sub>x</sub>, TiO<sub>2-y</sub>C<sub>y</sub> and TiO<sub>2-z</sub>S<sub>z</sub>, which will be discussed later.

Fig. 1B shows the wide energy range XPS spectra of TiO<sub>2-x</sub>N<sub>x</sub>, TiO<sub>2-y</sub>C<sub>y</sub> and TiO<sub>2-z</sub>S<sub>z</sub> before Ar<sup>+</sup> sputtering. The XPS binding energies from the samples were calibrated with respect to the C 1s peak from the carbon tape at 284.6 eV. For all doped TiO<sub>2</sub> samples, typical binding energies for Ti 2p and

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