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Effect of 3*d*-Metal Dopants on the Electronic Properties of Hexagonal Titanium Dioxide Nanotubes

E. P. D'yachkov*, D. V. Makaev, L. O. Khoroshavin, and P. N. D'yachkov

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia
*e-mail: evg_dyachkov@mail.ru
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Abstract—The electronic structure of hexagonal TiO_2 nanotubes doped with 3d transition metals from Sc to Zn was calculated by the linearized augmented cylindrical wave method. The calculated densities of states demonstrate that the substitution of Sc, V, Co, Cu, or Fe atoms for a part of Ti atoms leads to the decrease in the band gap width of the material from 4 to 2 eV. Such nanotubes are promising materials for creation of electrodes for electrochemical photolysis of water.

The discovery of the water splitting reaction at titanium dioxide electrodes [1] when irradiated with solar energy to produce hydrogen has become an important event in the development of electrochemical photolysis of water at semiconductor electrodes. Due to activity, high stability, nontoxicity, and low cost, titanium dioxide has attracted much recent attention as a photocatalytic material. Nevertheless, its application in the field of hydrogen energy and renewable energy sources is constrained by the large band gap width $E_g = 3.23$ eV of TiO_2 crystals. Because of this, the compound exhibits photocatalytic activity only when exposed to UV light, which accounts for about 5% of the solar energy; almost half of the solar energy is visible light. Thus, the question of how to efficiently extend the spectral response of titanium dioxide to the visible range is an extremely important problem of using this photocatalyst for more complete utilization of solar energy. Modification of the electronic band structure through doping TiO_2 crystals with main-group or transition elements is a possible way to extend the absorption edge of the material [2–5].

Doping can lead to the formation of an impurity bands in the crystal band gap, as well as to changes in the conduction or valence band; this can result in some narrowing of the band gap and improve photocatalytic activity characteristics of the material. In particular, calculations of the electronic structures of titanium dioxide crystals demonstrate that doping with V, Mn, Fe, Cr, Ni, Cu, Ag, and Au leads to the narrowing of the band gap [6–13]. Another possible way to improve the photocatalytic activity of TiO_2 is going from crystalline titanium dioxide to nanotubes, which

have a large surface area and high adsorptivity; TiO_2 nanotubes can be synthesized through a hydrothermal route or sol–gel process on carbon nanotube matrices [14–20]. It is expected that the transition to nanomaterials should lead to an adverse increase in the band gap width because of size effects; however, there is a hope to compensate for these effects by introducing extraneous species, for example, transition metal ions, using an ion-exchange technique. There are three structure types of TiO_2 nanotubes. By analogy with the formation of carbon nanotubes from a graphene sheet, they can be constructed by rolling up three-layer O–Ti–O sheets of rutile (110), anatase (101), or (111) hexagonal fluorite surfaces.

The aim of this study is to calculate the electronic structure of hexagonal TiO_2 nanotubes doped with 3d transition metals. All calculations were performed by the linearized augmented cylindrical wave (LACW) method for a (4,4) TiO_2 nanotube comprising 24 atoms (not very large number) per translational unit cell. Earlier, the stability and band structure of undoped single-wall and multiwall TiO_2 nanotubes based on the hexagonal structure, rutile, and anatase have been studied by ab initio quantum-chemical methods [21–25]. In addition, the effect of B, C, N, and S dopants on the electronic properties of such nanotubes, as well as the effect of Fe on the properties of an anatase-type TiO_2 nanotube, has been studied [26–31].
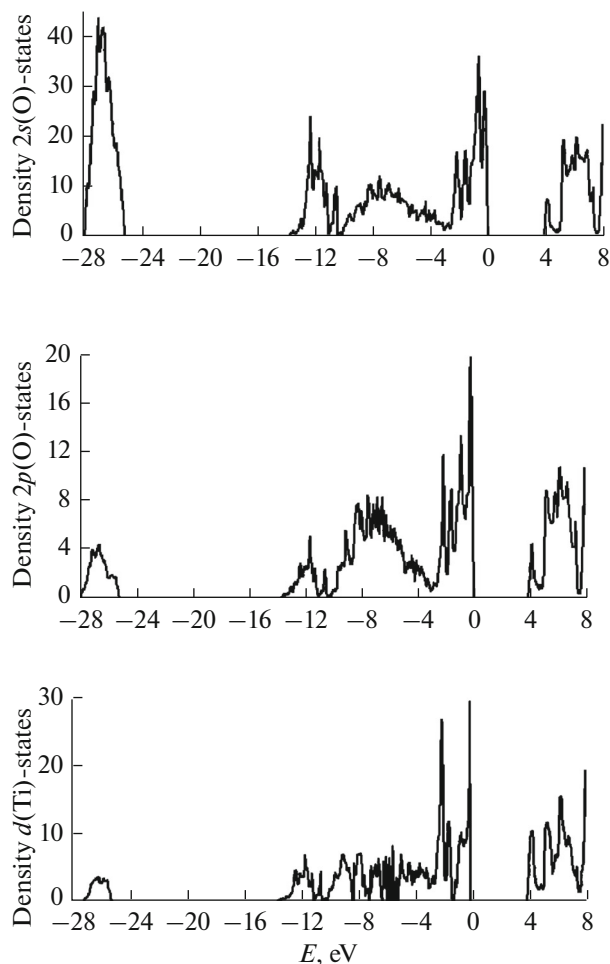
Fig. 1. Partial densities of states in the (4,4) TiO$_2$ nanotube.

COMPUTATIONAL DETAILS

The LACW method is an extension of the linearized augmented plane wave method to the case of simply periodic polyatomic systems with a cylinder or tube geometry. The method and its application to different nanotubes have been described in original papers [32–35] and reviews [36, 37]. Basic approximations used in this theory are the local density functional approximation and the muffin-tin approximation for the electron potential, which is taken to be spherically symmetric in the vicinity of atoms and constant in the interspherical space confined by two potential barriers separating a polyatomic cylindrical system from the vacuum regions outside and inside the tube. As a result, the electronic structure of nanotubes in the LACW method is determined by the free motion of electrons in the interspherical region, electron scattering on atomic spheres, and reflection from the bar-

riers. The method requires introducing one parameter, namely, the cylindrical layer width (Δ), which is common for the undoped and doped nanotubes. In this work, the parameter $\Delta = 4.06$ Å was selected in such a way that the band gap width in the initial TiO$_2$ nanotube was 4 eV. It should be noted that this Δ value is nearly the same as the van der Waals thickness of the TiO$_2$ layer so that the space confined between the barriers contains an essential part of the electron density of nanotubes.

RESULTS AND DISSCUSSION

Figure 1 shows the calculated partial densities of states for the initial (4,4) TiO$_2$ nanotube, and Fig. 2 shows total densities of states for this tube and nine doped nanotubes with one dopant atom in each unit cell, which corresponds to an impurity content of about 4 at %. In qualitative agreement with the electron distribution for the ionic model Ti^{4+}(O^{2-})$_2$, the valence band of titanium dioxide is formed by the narrow internal 2s(O) band with an electron binding energy of 25–28 eV and the 2p(O) band with a width of 13 eV near the top of this band, which is separated by a broad band gap from the conduction band formed by vacant 3d(Ti) orbitals.

It is seen that the substitution of one Ti atom by other 3d metals causes a noticeable change in the electronic structure of the nanotube. From the view point of photocatalytic applications, it is important that doping the TiO$_2$ tube with Sc, V, Co, or Cu leads to the formation of a new band with a width less than 0.5 eV in the center of the band gap so that the band gap width of the material decreases almost to 2 eV. In all cases, the introduction of a dopant is accompanied by the broadening of the valence and conduction band edges. This effect is especially pronounced in the Fe-doped compound for which an extended series of bands is formed near the bottom of the valence band so that the band gap also becomes half as large. The tubes doped with chromium or zinc should be nearly inert.

In addition to the band gap, doping leads to the perturbation of the valence and conduction bands. With an increase in the atomic number of a metal, the 2s(O) peak is shifted to the low-energy region by maximally 3 eV for Zn and its width increases by approximately 1 eV. Conversely, the 2p(O) band gradually decreases from 14 to 7–8 eV, and its shape, in particular, peak intensities, noticeably changes. This valence band changes can be detected by X-ray electron spectroscopy. The shape of the conduction band, including the peak number and intensity, is also sensitive to the nature of a 3d dopant.
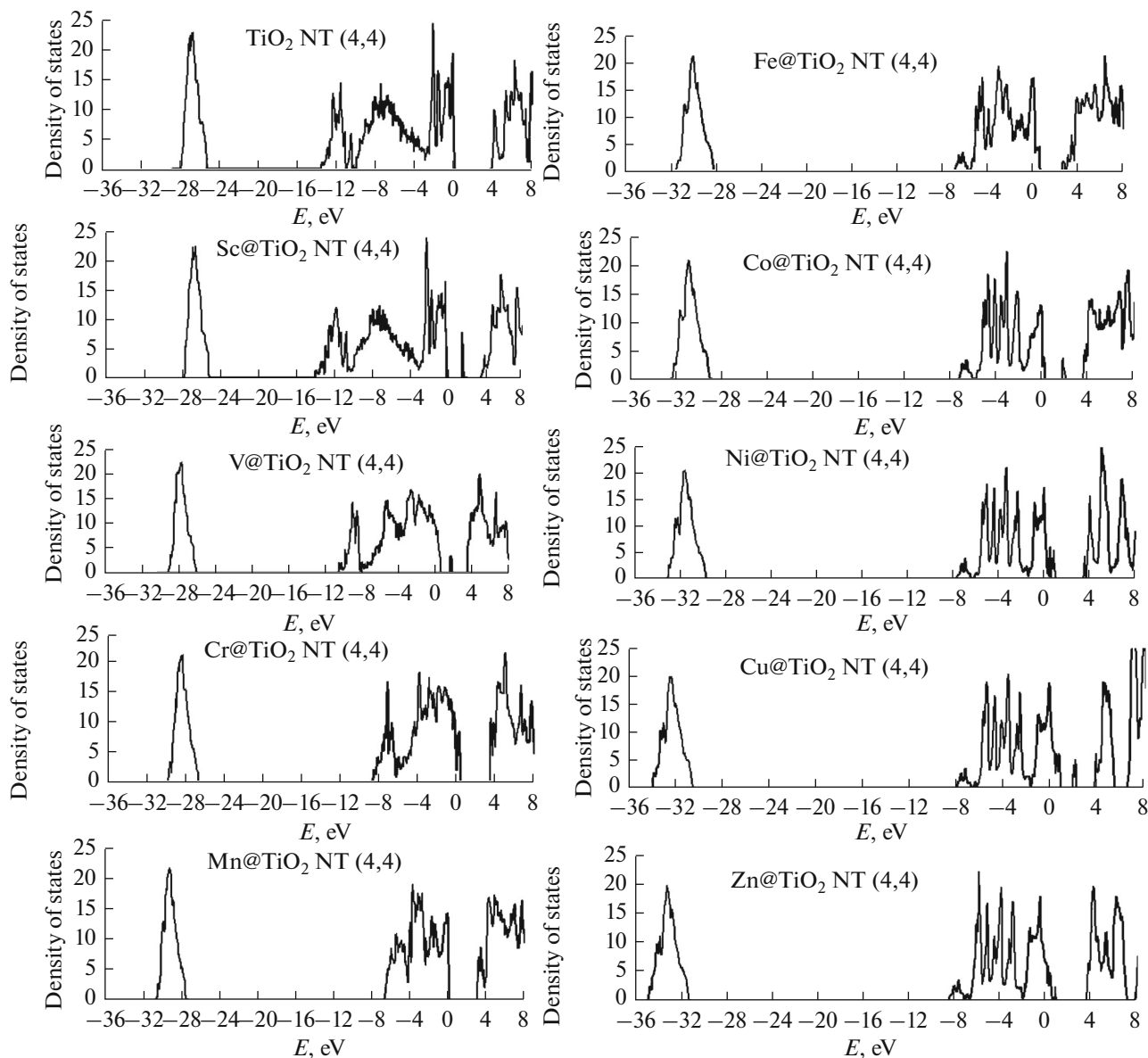
Fig. 2. Total densities of states in MTiO$_2$ containing one impurity atom M in a Ti position in unit cells of the (4,4) TiO$_2$ nanotube.

Thus, hexagonal TiO$_2$ nanotubes doped with 3*d* transition metals from Sc to Zn have been studied by quantum-chemical methods. The calculated densities of states demonstrate that the substitution of some Ti atoms by Sc, V, Co, Cu, and Fe leads to a decrease in the band gap width of the material from 4 to 2 eV. Such nanotubes are promising materials for design of electrodes for electrochemical photolysis of water.

ACKNOWLEDGMENTS

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